OSQ 83-00148

FINAL REPORT P-4321/G

Wet Oxidation of Produced Water Ancillary Fuels for Oilfield Applications

Phase I, Kinetics, Conceptual Designs and Economics

DSS File No. 15SQ.23440-3-9166

H. L. Robey, P.Eng.
Environmental & Chemical
Engineering Division

April 22, 1985.

ONTARIO RESEARCH
FOUNDATION

SHERIDAN PARK RESEARCH COMMUNITY

MISSISSAUGA, ONTARIO, CANADA L5K 1B3 • (416) 822-4111 • TELEX 06-982311

318 pp

MAY 0 3 1986
MICROMEDIA

WE, THE ONTARIO RESEARCH FOUNDATION, STIPULATE THAT THIS DOCUMENT IS SUBJECT TO THE FOLLOWING TERMS AND CONDITIONS:

1. ANY PROPOSAL CONTAINED HEREIN WAS PREPARED FOR THE CONSIDERATION OF THE ADDRESSEE ONLY. ITS CONTENTS MAY NOT BE USED BY NOR DISCLOSED TO ANY OTHER PARTY WITHOUT OUR PRIOR WRITTEN CONSENT.
2. ANY TESTING, INSPECTION OR INVESTIGATION PERFORMED BY US WILL BE CONDUCTED IN ACCORDANCE WITH NORMAL PROFESSIONAL STANDARDS. NEITHER WE NOR OUR EMPLOYEES SHALL BE RESPONSIBLE FOR ANY LOSS OR DAMAGE RESULTING DIRECTLY OR INDIRECTLY FROM ANY DEFAULT, ERROR OR OMISSION.
3. ANY REPORT, PROPOSAL OR QUOTATION PREPARED BY US REFERS ONLY TO THE PARTICULAR MATERIAL, INSTRUMENT OR OTHER SUBJECT REFERRED TO IN IT. NO REPRESENTATION IS MADE THAT SIMILAR ARTICLES WILL BE OF LIKE QUALITY.
4. NO REPORT ISSUED BY US SHALL BE PUBLISHED IN WHOLE OR IN PART WITHOUT OUR PRIOR WRITTEN CONSENT.
5. OUR NAME SHALL NOT BE USED IN ANY WAY IN CONNECTION WITH THE SALE, OFFER OR ADVERTISEMENT OF ANY ARTICLE, PROCESS OR SERVICE.
6. WE RESERVE THE RIGHT NOT TO COMMENCE AND/OR CONTINUE ANY WORK UNTIL PAYMENT ARRANGEMENTS SATISFACTORY TO US ARE ESTABLISHED.

TABLE OF CONTENTS

	Page No.
1. SUMMARY	1
2. BACKGROUND	3
2.1 Oil Sands Recovery	3
2.2 General Description of Wet Air Oxidation	6
3. OBJECTIVES	17
4. EXPERIMENTAL EQUIPMENT AND PROCEDURES	18
4.1 Analytical Procedures	18
4.2 Wet Oxidation Test Equipment	21
5. EXPERIMENTAL PROGRAMME RESULTS AND DISCUSSION	22
5.1 Produced Water	23
5.2 Coke Wet Oxidation Experiments	36
5.3 Athabasca Pitch	55
5.4 Asphaltenes	58
5.5 Mixed Coke/Produced Water	61
5.6 Vapour Phase Catalysis	64
5.7 Corrosion Tests	73
6. PATENT - HIGH THERMAL FLUX WET OXIDATION STEAM GENERATOR	130
6.1 Description of Invention	132
6.2 Summary	137
7. TECHNICAL AND ECONOMIC ASSESSMENT	140
7.1 General Description	141
7.2 Input Variables	144
7.3 Program Logic	146
7.4 Output Description	152
7.5 Results of Computer Evaluation	154
7.6 Economic Analysis Discussion	155
8. DISCUSSION AND IMPLICATIONS OF RESEARCH PROGRAM	189
9. SOLID FUEL/PRODUCED WATER WETOX$^{(R)}$ PILOT PLANT	194
9.1 Justification	194
9.2 Pilot Plant Description (Preliminary)	196
9.3 Preliminary Cost Estimate	198

TABLE OF CONTENTS (Contd.)

	Page No.
10. CONCLUSIONS	199
11. RECOMMENDATIONS	203
12. REFERENCES	204
APPENDIX A - 2 Litre Autoclave	207
B - 1-10 Continuous Flow Unit	211
C - Wetox$^{(R)}$ Continuous Flow Pilot Plant	216
D - Batch Test Conditions	227
E - 4-10 Fluid Coke Discussion	241
F - Letter to Phillips Petroleum	251
G - Canada Patent Application	254
H - Computer Program Listing	272
I - Options 1 - 6, Base Case Results Printouts	280

TABLE OF CONTENTS (Contd.)

Page No.

LIST OF TABLES

Table 5.1 - Produced Water Sample Analyses 78
5.2 - PW-1 Kinetics: No Additions 79
5.3 - Arrhenius Parameters 80
5.4 - Kinetics of PW-1: Copper Catalyst & pH Adjusted Runs 81
5.5 - Arrhenius Parameters 82
5.6 - Arrhenius Parameters - "Other" Produced Water Samples 83
5.7 - Single Compartment Continuous Flow Test 84
5.8 - 4-Compartment Reactor Test Conditions 85
5.9 - Produced Water - Pilot Plant Test Results 86
5.10 - 4-Compartment Reactor Test Conditions 87
5.11 - Delayed Coke Sample Analyses 88
5.12 - Delayed Coke - Comparison of Sulfur & Carbon Oxidation Kinetics 89
5.13 - Delayed Coke Kientics No Additions (100 mesh) 90
5.14 - Delayed Coke - Arrhenius Parameters (No Addition) 91
5.15 - Kinetics of Fluid Coke No Addition 92
5.16 - Fluid Coke - Effect of Particle Size on Arrhenius Parameters 93
5.17 - Athabasca Pitch Kinetics No Additions (100 mesh) 94
5.18 - Athabasca Pitch - Arrhenius Parameters 95
5.19 - Arrhenius Parameters Asphaltines 96
5.20 - Mixed Waste Kinetics - 280°C 97
5.21 - Mixed Waste - Arrhenius Parameter 98
5.22 - PtO_2 Catalyst - Run #1 Results 99
5.23 - PtO_2 Catalyst - Run #2 Results 100
5.24 - Copper Oxide Catalyst Results 101
5.25 - Copper Oxide - HSCA & Usp 102
5.26 - Iron Oxide Catalyst Results 103
5.27 - Corrosion Test Results 104

TABLE OF CONTENTS (Contd.)

Page No.

Table 7.1 - Option 1 Base Case Cost Summary 165
7.2 - Option 1 Sensitivity Variable Summary 166
7.3 - Option 2 Base Case Cost Summary 167
7.4 - Option 3 Base Case Cost Summary 168
7.5 - Option 3 Sensitivity Variable Summary 169
7.6 - Option 4 Base Case Cost Summary 170
7.7 - Option 4 Sensitivity Variable Summary 171
7.8 - Option 5 Base Case Cost Summary 172
7.9 - Option 6 Base Case Cost Summary 173
7.10 - Option 6 Sensitivity Variable Summary 174

TABLE OF CONTENTS (Contd.)

Page No.

LIST OF FIGURES

Figure 2.1 - General Process Schematic 12
2.2 - Effect of Temperature on Combustion 13
2.3 - Effect of Stirring 14
2.4 - Concentration-Time Profile 15
2.5 - Wetox(R) Process Schematic 16

5.1 - PW-1 Kinetics (Injection) 105
5.2 - Arrhenius Plot - PW-1 (No Additions) 106
5.3 - PW-1 Effect of Additions at 260°C 107
5.4 - Arrhenius Plot - Effect of Addition (PW-1) 108
5.5 - Arrhenius Plot - "Other" Produced Water Samples 109
5.6 - Delayed Coke - 240°C 110
5.7 - Delayed Coke - 260°C 111
5.8 - Delayed Coke - 280°C 112
5.9 - Delayed Coke Kinetics 240°C and 290°C 113
5.10 - Delayed Coke - Arrhenius Plot 114
5.11 - Delayed Coke - Effect of NaOH on Rate Constant at 260°C 115
5.12 - Delayed Coke - Effect of O_2 Pressure at 260°C 116
5.13 - Fluid Coke Kinetics 240, 260, 280°C 117
5.14 - Fluid Coke Kinetics 300, 320°C 118
5.15 - Effect of Preheat and Surfactant Addition on Fluid Coke Oxidation (260°C) 119
5.16 - Arrhenius Plot - Fluid Coke 120
5.17 - Effect of O_2 Pressure 121
5.18 - Athabasca Pitch Kinetics No Additions 122
5.19 - Athabasca Pitch Kinetics No Additions - 320°C 123
5.20 - Athabasca Pitch - Arrhenius Plot 124
5.21 - Asphaltines Reaction Kinetics Effect of Copper Catalyst, 280°C 125
5.22 - Asphaltines Arrhenius 126
5.23 - "Mixed Waste" Kinetics (280°C) 127
5.24 - "Mixed Waste" Arrhenius 128
5.25 - Vapour Phase Catalysis System 129

TABLE OF CONTENTS (Contd.)

Page No.

Figure 6.1 - Mass/Energy Flow Schematic 139

7.1 - Option No. 1 175
7.2 - Option No. 2 176
7.3 - Option No. 3 177
7.4 - Option No. 4 178
7.5 - Option No. 5 179
7.6 - Option No. 6 180
7.7 - Option No. 1 Mass and Energy Balances 181
7.8 - Option No. 4 Mass and Energy Balances 182
7.9 - Option No. 1 Sensitivity Analysis 183
7.10 - Option No. 4 Sensitivity Analysis 184
7.11 - Option No. 3 Mass and Energy Balances 185
7.12 - Option No. 6 Mass and Energy Balances 186
7.13 - Option No. 3 Sensitivity Analysis 187
7.14 - Option No. 6 Sensitivity Analysis 188

Wet Oxidation of Produced Water Ancillary Fuels for Oilfield Applications
Phase I, Kinetics, Conceptual Designs and Economics

(Final Report P-4321/G)

DSS File No. 15SQ.23440-3-9166

1. SUMMARY

An extensive experimental program was undertaken to examine the application of wet air oxidation, specifically the Wetox$^{(R)}$ process to oil sand recovery operations. Batch scale experiments were conducted on the following:

- Produced Waters
- Delayed Coke
- Fluid Coke
- Eureka Process Pitch
- Asphaltenes

The oxidation reaction kinetics of these were modelled assuming first order reactions. The oxidation reactions of the produced waters tested were analagous to those of many organic materials, in that the oxidation rate inflected from a fast regime at about 50-75% conversion to a slow regime. With the solid fuels, however, rapid reaction proceeded until greater than 90% of the initial organic material was oxidized. Solid fuels are, therefore, particularly attractive candidates for wet oxidation.

Continuous flow pilot scale tests were attempted using produced water and fluid coke. Although limitations in operating temperature and pressure in the unit precluded obtaining acceptable kinetic data, a number of potential practical problems with the operability of the system were identified.

A modification to the wet oxidation reactor was conceptualized during the research, which allows for extremely high energy output per unit reactor volume. This now patented modification results in versatility of application with lower capital and operating costs as compared to the unmodified systems.

A computer aided technical and economic assessment validated a considerable number of options for the application of wet air oxidation in oil sand recovery operations. The cost of high pressure injection steam for in-situ recovery operations was desirable, the cost was calculated to be $6.14/GJ (air based system).

For Thermal energy, in the form of high temperature water or process steam, with a credit given to relatively pure carbon dioxide as by-product, the cost was determined to be $2.79/GJ (pure oxygen based system).

Recommendations for future development of the process are discussed. The major step would be to construct and operate a suitable pilot scale facility designed for the application.

H. L. Robey, P.Eng.
Mamager, Wet Oxidation Technology
Environmental & Chemical
Engineering Division

HLR/id
April 22, 1985

2. BACKGROUND

2.1 Oil Sands Recovery

The vast oil sands deposits in Western Canada represent enormous potential for the country in striving to attain energy self sufficiency. They are not an easy resource to tap as the bitumen is extremely viscous, and is enveloped in a semi-rigid matrix of sand and water. Technologies for releasing the bitumen have been under investigation for decades throughout the world, mostly in Northern Alberta. Therefore, Canada, in particular Alberta, is the world leader in its development.

There are various technologies for recovering bitumen from oil sand deposits. For the most part, selection of a particular process is site specific, dependent, primarily, on depth of deposit. Oil sands lying within 50 metres of the surface are economically mineable, while suitably deep deposits are subjected to in-situ recovery techniques.

Commercial surface mining of oil sands has been in operation for a number of years in the Athabasca deposit close to Fort McMurray, Alberta. The two large plants, operated by Suncor Inc. and Syncrude Company Ltd. (consortium) have been in operation since 1967 and 1977 respectively and have bitumen recovery as well as primary upgrading processes. Both of these complexes employ the Clark hot water process for extraction of the raw bitumen from the sand, silt and clay impurities.

In-situ bitumen recovery processes are not as far advanced as the oil mining type systems. There are a considerable number of pilot plant experimental operations in Athabasca, Cold Lake and Peace River. Several companies have recently announced the commercialization of pilot scale systems operations.

At the reservoir conditions, the raw bitumen is too viscous to be pumped to the surface using conventional oilfield equipment. In general, there are two types of processing schemes which reduce the viscosity of the oil to a pumpable state:

1. Thermal Processes
2. Non Thermal Processes

There are many thermal recovery projects at various stages of development in Venezuela, the United States, and, most significantly, Western Canada. The most promising to date are steam based processes, and, to a lesser degree, in-situ combustion. Thermal processes are significantly further advanced than non thermal processes which include injection of emulsifiers, hydrocarbon solvents, and/or combustion gases with or without simultaneous steam injection.

Both the oil sand mining/extraction and steam based in-situ techniques are very energy intensive. To meet this demand, a number of candidate fuels are available. These are, in increasing order of preference with respect to maximization of liquid yield and ancillary "effective" conversion of alternate and preferentially low quality fuels to premium transportation fuels:

- produced bitumen
- natural gas
- coal
- bitumen upgrading residues

The Suncor Inc. and Syncrude mining plants currently employ delayed and fluid coking respectively for upgrading of the raw bitumen. The largest by-product of both processes is coke, which is high in sulfur and heavy metals contents. Conventional combustion of these low grade by-products is limited, due to the excessive release of sulfur dioxide to the atmosphere without flue gas desulfurization being applied. As a consequence, considerable volumes of coke are currently being stockpiled.

In the steam stimulation type processes, it has been reported that approximately one barrel of oil (energy equivalent) out of every three barrels produced is required for steam raising. Currently, steam is producted generally by once through steam generators, which are fuelled by natural gas or produced crude oil. In view of the fact that both natural gas or crude oil have a limit on long term availability, efforts are being made to utilize upgrader residues or other solid fuels for steam generation.

Besides the considerable fuel demand, the required steam generation also requires large volumes of softened oil free water. Some of the brackish produced water can be recycled, however, it must be extensively treated to meet conventional boiler feedwater specifications. There is also considerable environmental pressure to maximize reuse, as there is a limited supply of fresh make-up water.

In 1982, a study was completed by CH2M Hill Canada Ltd. for The Canada Centre for Mineral and Energy Technology (CANMET), Energy, Mines and Resources Canada (EMR), entitled "Generation of Steam Using Low-Grade Fuels and Field Produced Water for In-situ Oil Recovery"(1). One of the objectives of that work was to evaluate potential steam generation technologies which may be applicable to in-situ thermal recovery operations. Wet air oxidation was determined to have the greatest potential, largely due to the fact that produced water pretreatment is not required and low grade solid fuels can be employed as the energy source. This research program was initiated as a follow-up to the CH2M Hill study to evaluate the fundamental reaction characteristics of the wet oxidation process, and to assess its feasibility in oil sands recovery operations.

2.2 General Description of Wet Air Oxidation

Wet air oxidation is a process in which combustible material is oxidized by air or oxygen in the presence of liquid water. Elevated temperatures are required to achieve a useful reaction rate and, therefore, to maintain a liquid phase, elevated pressures are required. The process is operated continuously with liquid and gas streams being introduced to the reactor simultaneously.

A basic flowsheet for the process is presented in Figure 2.1. The waste is pumped via a high pressure pump through a heat exchanger and then into a reactor where it is mixed with compressed air. The oxygen in the air reacts with the organic matter in the slurry to produce mainly carbon dioxide and water. The exothermic nature of the reaction produces heat which raises the temperature of the reactor contents. The effluent from the wet oxidation reactor is heat exchanged with the incoming waste.

Almost any oxidizable material which remains in the liquid phase can fuel the process. The direct destruction of organic contaminants in water at elevated temperature and pressure to raise steam is a realistic and attractive alternative to concentration and incineration of a dry residue. In either case, the products are the same: carbon dioxide, water and ash. Since the products from wet air oxidation are automatically and thoroughly scrubbed, air and odour pollution are minimized. In addition, if an organic waste or solid fuel contains appreciable concentrations of sulfur, chlorine or nitrogen, extensive flue gas treatment equipment is not required. In wet oxidation, sulfur is converted to sulfuric acid, chlorine to hydrochloric acid and nitrogen often forms ammonia. All are retained in solution as acid or base, however, if appropriate cations are present, salts will be formed.

The wet air oxidation process provides an efficient means for the recovery of the energy from relatively dilute waste streams. The reaction occurs and the energy is liberated in the liquid phase, with no barrier to the transfer. The energy can, therefore, be recovered with the highest degree of efficiency.

2.2.1 Physical Parameters Governing Wet Oxidation

The maximum extent of the oxidation is primarily a function of the maximum operating temperature within the reactor. A typical combustion curve is presented in Figure 2.2 The operating temperature effectively dictates the minimum operating pressure since confinement of the resulting steam and adequate oxygen partial pressure is required.

In wet air oxidation, oxidation and hydrolysis reactions proceed simultaneously, depending on the effective availability of oxygen. Thus, with inadequate transfer of oxygen, hydrolysis reactions become significant and often generate products which are refractory to further oxidation in this process. Examples of these products are low molecular weight carboxylic acids; acetic, propionic, etc. The mass transfer requirements must, therefore, be satisfied to achieve maximum conversions to carbon dioxide and water. The rate of transfer of oxygen into the solution at a given operating temperature is controlled by:

- The solubility of oxygen in the waste which is a function of the oxygen partial pressure or over-pressure. Increased process pressures will, therefore, result in increased rates of mass transfer.

- The degree of mixing of the oxygen and the organic material.

- The rate of removal of reaction products and of heat transfer on a microscopic scale.

Increased process pressures result in increased capital costs for the reactor vessel, heat exchanger, compressor, etc., as well as increased operating costs, largely attributable to electrical power consumption. Effective mixing is, therefore, a most important parameter in economically optimizing the system, as shown in Figure 2.3.

The process temperature and pressure are also critical in determining mass and energy balances around the wet oxidation system. Specifically, these parameters, along with oxidant feedrate, control the quantity of liquid that is evaporated during reaction. The amount of steam which is produced per unit of product gases is called the absolute humidity ratio, which is calculated as follows:

$$HR = \frac{MW_L \times P_V}{MW_G\,(P - P_V)}$$

where:
HR - Humidity ratio (wt steam/wt gas)
MW_L - Molecular weight of liquid
MW_G - Molecular weight of gas
P_V - Vapour pressure of water at temperature
P - Total reactor pressure

All in consistent units.

2.2.2 Reaction Kinetics

It has been demonstrated previously with many organic materials, that the extent of destruction of organics (as measured by chemical oxygen demand - COD) can be represented by two first order reactions in series. Therefore, by plotting the natural logarithm of the chemical oxygen demand (COD) against residence time, two straight lines are apparent. Mathematically, this is represented as follows for each of the two regimes:

$$\ln \frac{C_t}{Co} = {}^{-}kt$$

where: C_t = organic concentration as measured by COD at "t"

Co = COD at time = 0

k = specific reaction rate constant for first or secondreaction (min^{-1})

t = residence time (mins)

The first reaction is usually one to two orders of magnitude greater than the second. The initial regime is considered to be a combination of many simultaneous reactions including complete oxidation to carbon dioxide and water, partial oxidation generating the refractory organic species and competing hydrolysis reactions. Figure 2.4 shows a concentration time profile for the wet oxidation of a "typical" organic material. As the COD of the starting material is rapidly decreasing, refractory, low molecular weight species are being produced. When these partially oxidized by-products become predominant, their oxidation reaction rate will become the rate determining step.

The temperature influence on the first reaction can generally be ascertained quite well using the classical Arrhenius equation. This equation is a follows:

$$K = Ae^{-E/RT}$$

where:
K = rate constant (min^{-1})
A = frequency factor (min^{-1})
E = activation energy (cal/mole)
R = gas constant (cal/mole/K)
T = absolute temperature (K)

Therefore, a plot of natural log of K versus inverse absolute reaction temperature yields a straight line, with slope = activation energy/R and ordinate intercept = frequency factor.

Very small changes in organic concentration with time frequently preclude obtaining good correlation for the second regime, and, therefore, the temperature dependence is not as evident.

In energy recovery applications of wet air oxidation, only the first, rapid reaction is critical. To minimize reactor capital, it is most cost effective to limit the residence time to the inflection point between the two regimes, and apply a suitable safety margin.

2.2.3 The Wetox$^{(R)}$ Process

The heart of the Wetox$^{(R)}$ process (see Figure 2.5) is the reactor: a multi-compartmented horizontal unit with agitation and oxygen addition in each compartment. This design results in substantially increased reaction rates and makes possible efficient operation at relatively modest temperatures and pressures of approximately 230^{o}C and approximately 4 MPa (0.6 kpsi).

The liquid and steam phases are withdrawn separately from the reactor. This feature improves the heat exchange efficiency, increases the effective retention time of the liquid, and reduces the volume of liquid effluent for chemical recovery or treatment.

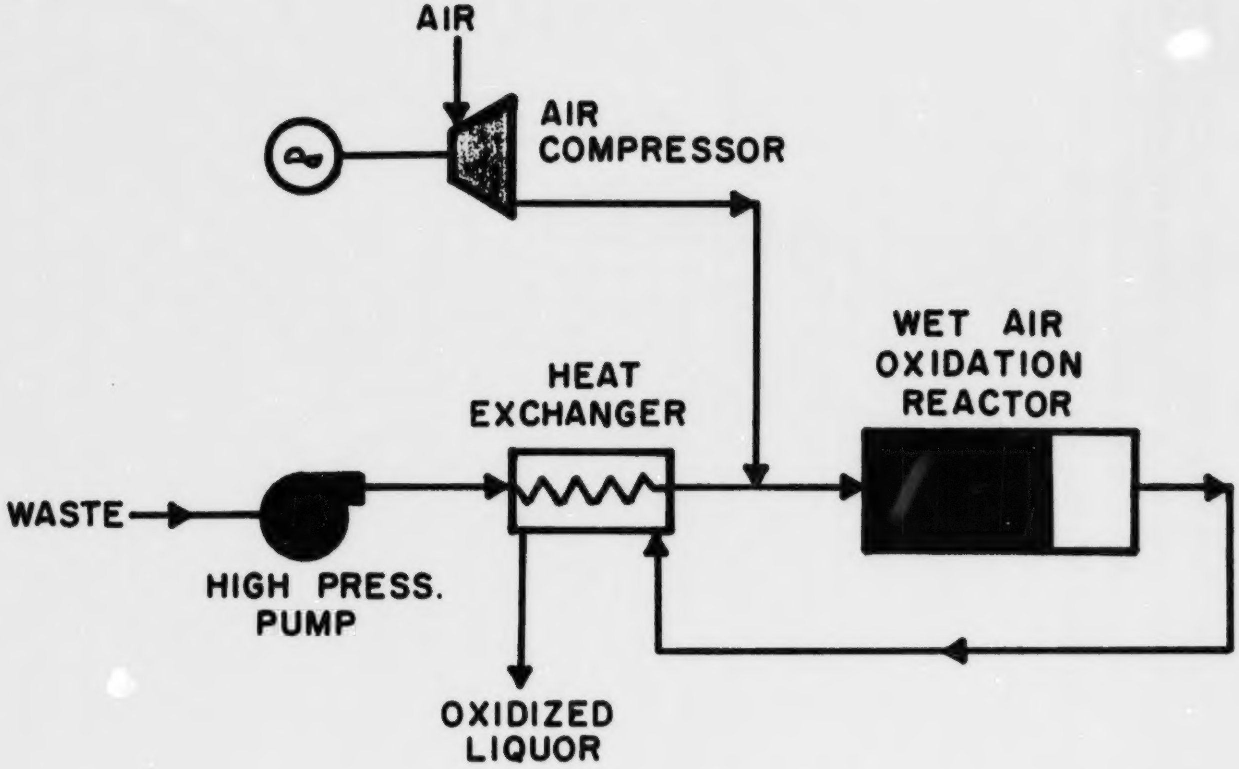
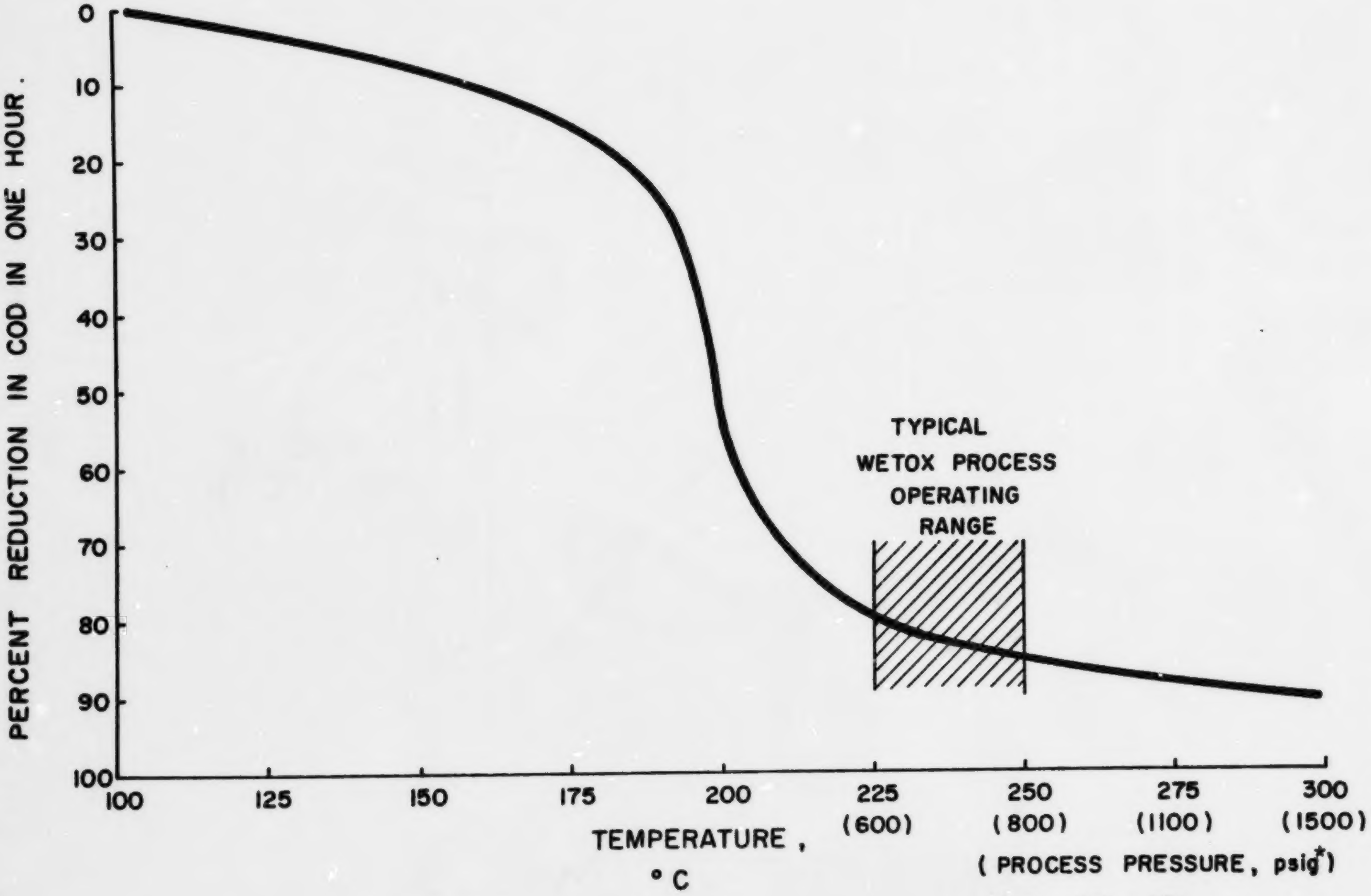

AIR
AIR COMPRESSOR
WASTE
HIGH PRESS. PUMP
HEAT EXCHANGER
WET AIR OXIDATION REACTOR
OXIDIZED LIQUOR

FIGURE 2.1 GENERAL PROCESS SCHEMATIC



*psi = 145 x MPa

FIGURE 2.2 EFFECT OF TEMPERATURE ON COMBUSTION

FIGURE 2.3

EFFECT OF STIRRING

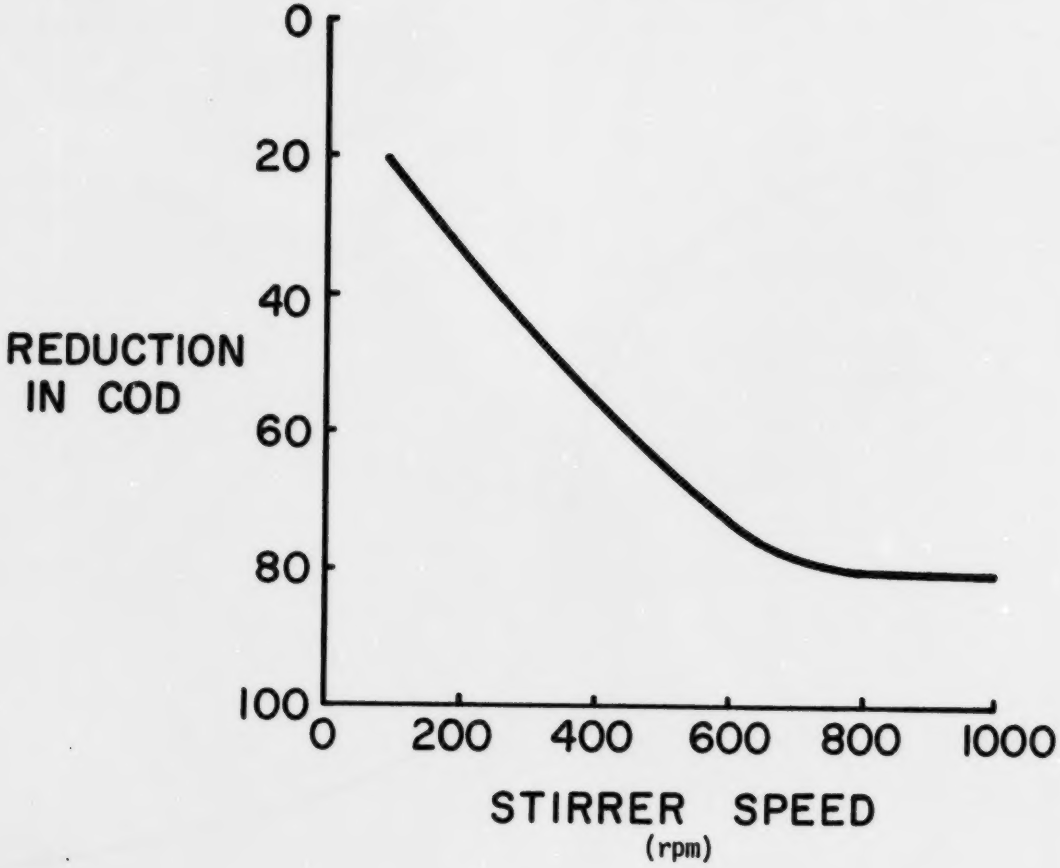
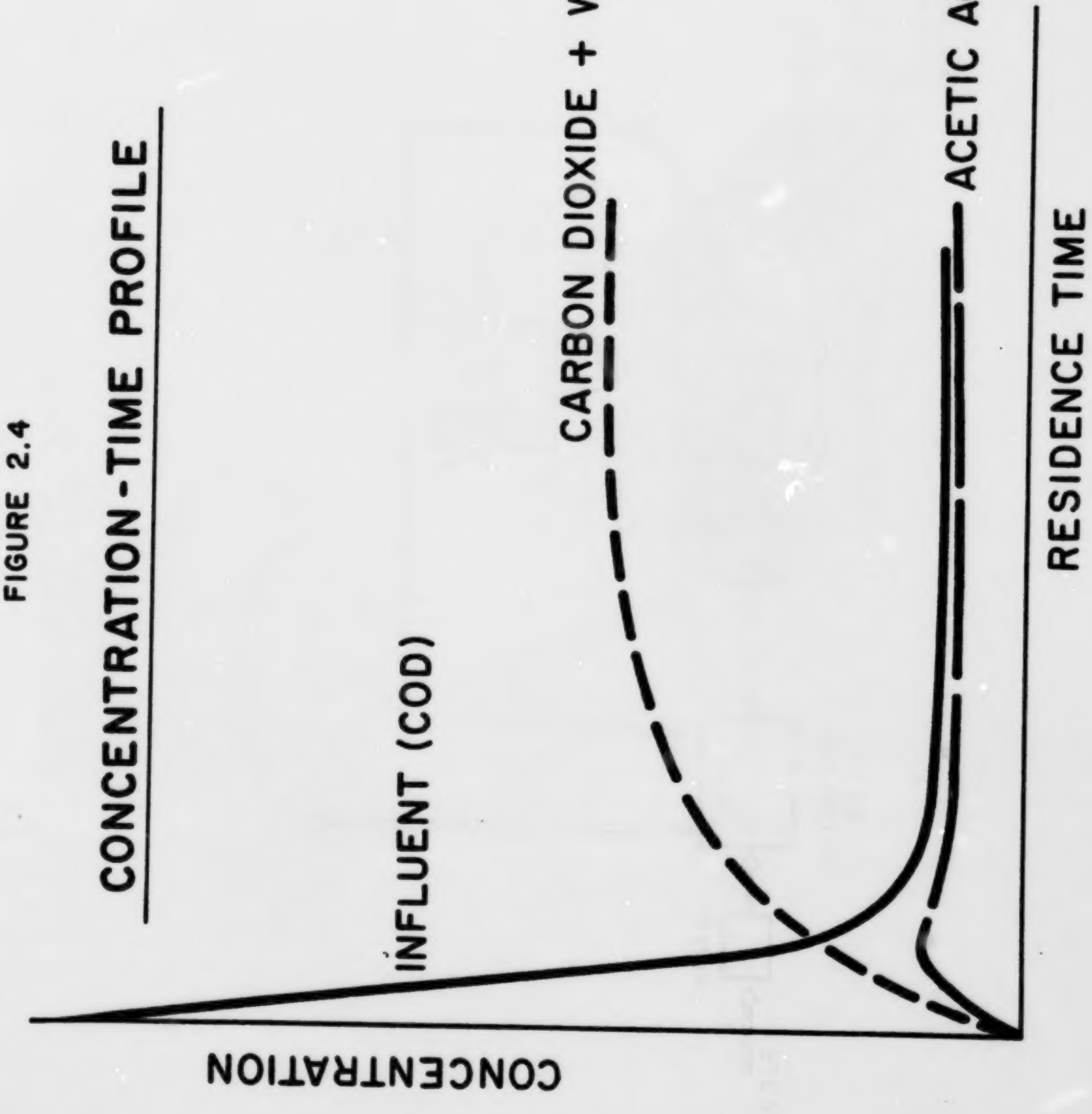


FIGURE 2.4

CONCENTRATION-TIME PROFILE



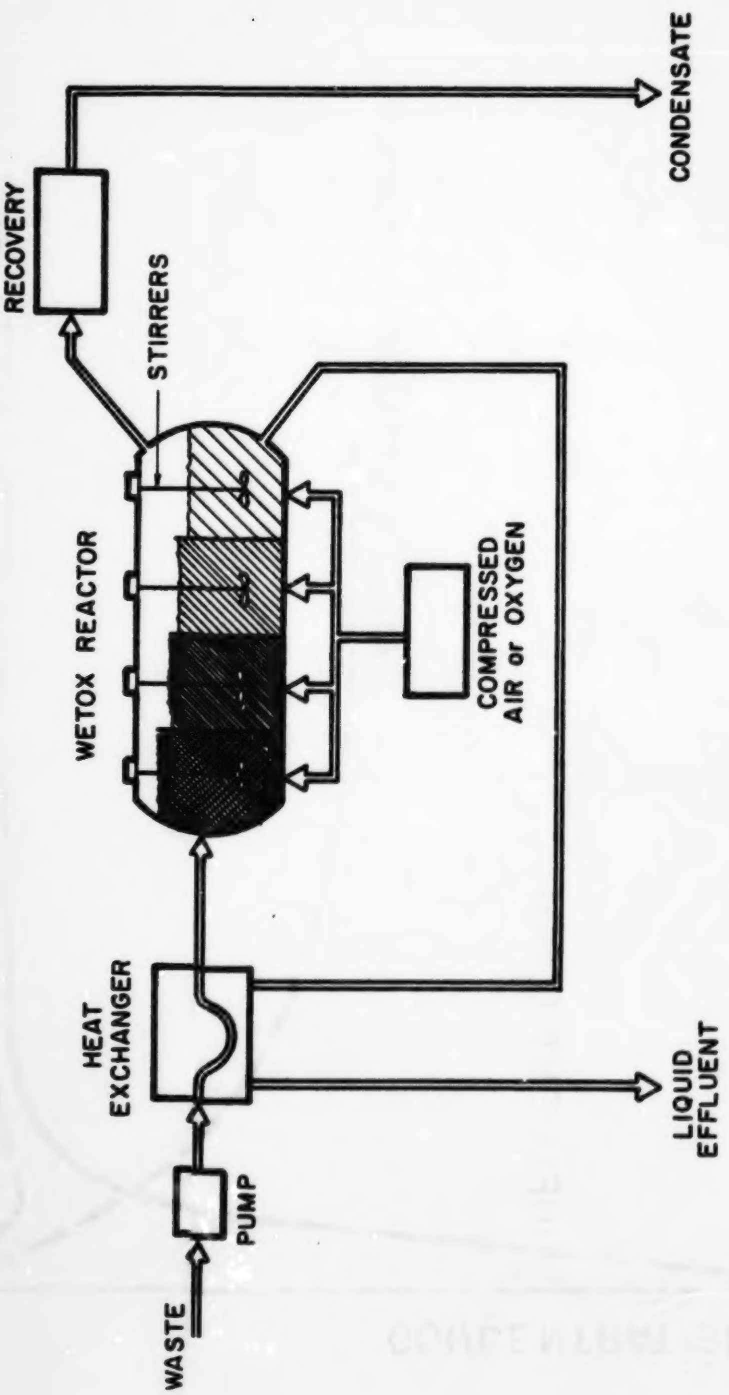

WASTE
PUMP
HEAT EXCHANGER
LIQUID EFFLUENT
WETOX REACTOR
STIRRERS
COMPRESSED AIR or OXYGEN
HEAT RECOVERY
CONDENSATE

FIGURE 2.5 WETOX® PROCESS SCHEMATIC

3. OBJECTIVES

The major objectives which were addressed in this research program were:*

1. Develop wet oxidation kinetics and an understanding of operating parameters for the treatment of solid or residual fuels and produced water slurries for direct energy recovery suitable to oil field requirements.

2. Develop design parameters and concepts for the wet oxidation process, and any necessary ancillary equipment, to treat produced water and ancillary fuels for recovery of bitumen and heavy oil.

3. Conduct a preliminary assessment of the comparative economics of selected options for application of wet oxidation.

4. Prepare a targeted, justified programme for continuation of the process' development in the application.

* Selective desulfurization of high sulfur petroleum residuals via wet oxidation, was a secondary objective in the work.

4. EXPERIMENTAL EQUIPMENT AND PROCEDURES

4.1 Analytical Procedures

The analytical procedures employed during this research are discussed in the following:

(i) Chemical Oxygen Demand (COD)

Reference: Water Pollution Control, May/June, 1978, pp 25-29, Knechtel, J. Ross.

A representative aliquot of sample was refluxed with $K_2Cr_2O_7$ and 50% H_2SO_4 solution in a sealed tube at 150°C for two hours. Ag_2SO_4 was added as a catalyst and $HgSO_4$ added to prevent chloride interference. After cooling, the increase in CrIII was measured spectrophotometrically at 600 nm.

(ii) Total Organic Carbon (TOC)

Reference: Standard Methods for the Examination of Water and Wastewater, 15th Edition, 1980. Method No. 505

An aliquot of sample was acidified and sparged with nitrogen to remove inorganic carbon. Total organic carbon was then determined by combustion infrared using a Beckman Model 915A Carbon Analyzer and Model 865 Infrared Analyzer.

(iii) Chloride

Reference: Standard Methods for the Examination of Water and Wastewter, 15th Edition, 1980. Method No. 407C.

Chloride was determined by potentiometric titration of an acidified aliquot of sample with standardized $AgNO_3$ solution. A silver-silver sulfide electrode was used in conjunction with a double junction reference electrode and a Beckman Model 601 Ion analayzer.

(iv) Total Solids and Ash

Reference: Standard Methods for the Examination of Water and Wastewater, 15th Edition, 1980. Method No. 209A & E.

An aliquot of sample was dried at 103°C to constant weight and residue on evaporation determined by difference. The dried residue was then ignited at 600°C (950°C for starting coke samples) to constant weight and residue on ignition reported as % ash.

(v) Total Suspended Solids and Volatile Suspended Solids

Reference: Standard Methods for the Examination of Water and Wastewater, 15th Edition, 1980. Method No. 209D & CE.

An aliquot of sample was filtered, using vacuum, through a tared 1.5 micron glass fiber disc (pre-fired at 600°C) and the residue remaining on the disc, after twenty-four hours in a convection oven at 103°C, was measured gravimetrically. The disc and dried solids were then ignited at 600°C for one hour and loss of ignition reported as volatile suspended solids.

(vi) Oil and Grease

Reference: Standard Methods for the Examination of Water and Wastewater, 15th Edition, 1980. Method No. 503A (liquids) or 503D (sludges).

An acidified aliquot of sample was sequentially extracted with 1,1,2-trichloro-1,2,2-trifluoroethane (freon). After evaporating the combined "freon" extracts at 25°C and purging with nitrogen to remove residual "freon", the residue was measured gravimetrically.

(vii) Sulfate

Reference: American Society for Testing Materials, Annual Book of Standards, 1983, Section 11, Volume 11.01, Water (D). Proposed test method for "Anions in Water by Ion Chromatography", page 696.

Direct injection of a filtered aliquot of sample into the anion system of a Dionex Model 16 Ion Chromatograph under "standard" conditions using conductivity detection.

(viii) Metals

Produced water "feed" samples were initially digested with concentrated aqua regia. Further treatment was carried out using sulfuric and perchloric acids prior to analysis using DC plasma emission spectrophotometry.

Wetox liquid effluents were acidified and analyzed directly using DC plasma emission spectrophotometry.

4.2 Wet Oxidation Test Equipment

4.2.1 Batch Units

The bulk of the batch testing was conducted in a 2-litre titanium autoclave. This unit is capable of a temperature of up to 290°C with a maximum operational pressure of approximately 9.65 MPa (1,400 psi).

A complete description of this unit is given in Appendix A.

A small number of the batch tests were conducted in a Hastelloy C-276 2-litre autoclave. This unit is similar to the titanium batch autoclave in operation, but is capable of temperatures to 320°C with a maximum operational pressure of approximately 17.2 MPa (2,500 psi).

4.2.2 Continuous Flow Units

Two units are available at Ontario Research for continuous flow pilot scale testing. The first is a small 5 L (active) volume titanium clad system, capable of operation to about 240°C and 4.6 MPa. A complete description of this unit is found in Appendix B.

A 50 L volume unit is also employed. This solid titanium unit, divided into 4 compartments, is capable of operation to about 250°C at 4.8 MPa (700 psi). Further description of the operation of this unit is provided in Appendix C.

5. EXPERIMENTAL PROGRAMME RESULTS AND DISCUSSION

Six different types of wastes/fuels were tested in the wet air oxidation systems at Ontario Research. These are presented in individual sections as follows:

5.1	Produced Waters
5.2	Delayed Coke
5.3	Fluid Coke
5.4	Eureka Pitch
5.5	Asphaltenes
5.6	Mixed Coke/Produced Water

5.1 Produced Water

Oil and water are separately, and in emulsion form, pumped to the surface from steam stimulation, in-situ oil recovery operations. Following naphtha and/or demulsifier addition, these produced fluids are processed in an interceptor or skim tank for gross oil-water- solids separation. Three phases exit from this unit operation, viz. oil froth, which is subsequently purified as product; solids, which are removed periodically for disposal; and the water phase, known as produced water. As it is desirable to reuse this water for steam injection, it is necessary to extensively treat it to boiler feedwater specifications. This entails removal of residual oils, softening, deaeration and polishing dissolved solids.

The objective of employing wet oxidation to the treatment of produced water is to eliminate, or minimize, the many unit operations currently utilized for its systematic treatment. Residual oils and soluble organics contained in the produced water, plus added solid by-product fuels (e.g. coke, pitch, etc.) would be combusted by wet air oxidation, and, through the evolution of heat, effect evaporation. The vapour so produced could either be injected directly into the oil bearing formation, or it could be condensed, separated from spent combustion gases and used as hot boiler feedwater. Contaminants contributing to the water hardness (e.g., calcium, magnesium) would be concentrated in the liquid phase effluent.

5.1.1 Waste Description

A variety of produced water samples was collected for wet oxidation testing. Most samples were obtained from Texaco Canada Inc.'s Athabasca site and one sample was obtained from Esso Canada's Cold Lake deposit. Both companies currently operate steam stimulation pilot plants at their respective deposits. Table 5.1 lists the produced waters collected and selected analyses performed.

Much of the fundamental testing was conducted using Texaco produced water, referred to as PW-1 in Table 5.1. A number of 1 litre containers of emulsion were received, each collected from a different Texaco well. These were visually classified and mixed according to high and low oil content and labelled as PW-1 and PW-2 respectively in Table 5.1. An aliquot was taken from each of these two waste samples without disturbing the separated heavy oil. These are referred to as Aqueous PW-1 and PW-2 in the Table. HTS and P-34 are Athabasca produced water samples, and the designated CLPW is from Cold Lake.

Analyses of the produced water samples, particularly oil and grease (Freon extractables), have to be considered with caution. Although samples were evidently shipped as true oil:water emulsions, there was a significant amount of free oil found in each which was either floating, precipitated or adhering to the container walls. It was difficult, therefore, to obtain representative aliquots for analyses or, indeed for individual experiments.

5.1.2 Batch Tests

The heterogeneous distribution and separation of bitumen in the produced water created many problems during batch scale wet oxidation tests. When the produced water was injected into the batch reactor at the desired temperature, the free bitumen coated the reactor internals. This material subsequently solubilized at a rate dependent upon reaction temperature, resulting in an apparent increasing organic concentration being measured in samples of the reacting solution.

Low concentration of a surfactant (sodium alkyl aryl sulfonate) was added to attempt to emulsify the mixture, with little success. Bentonite at a concentration of 5 g/L was found to be effective, however, probably because of its emulsifying properties. This addition, therefore, was utilized in all subsequent produced water batch tests.

COD analyses were used extensively to monitor performance and determine the reaction kinetics during the test program. Despite the handling problems encountered with the produced water, the COD data were reproducible and correlated well using the bentonite clay addition.

5.1.2.1 PW-1 Test Results

(i) No Additions

The first series of batch wet oxidation tests was conducted on Athabasca produced water (PW-1) as received, without additives, to assess the effect of temperature, and, therefore, allow a prediction of the system activation energy. The temperature range studied was 200 to 290°C. Samples were withdrawn at various times during each reaction and analyzed for COD content. These data were plotted using linear regression assuming first order kinetics for calculation of specific reaction rate constants and correlation coefficients calculated. A listing of the test conditions for all experiments is given in Appendix D.

A correlation coefficient (r) of 0.95 was arbitrarily selected as a measure of the quality of the experimental results. Runs yielding data with coefficients below this set point were duplicated. This performance criterion could not be met with data generated during tests at 220°C and below, and, therefore, these were not included in the kinetic analysis.

A plot of logarithmic COD versus reaction time is presented in Figure 5.1 for runs conducted at four different temperatures. For these experiments, aliquots of the produced water were injected into the batch reactor at temperature. Some tests were also conducted on PW-1, where the sample aliquot was placed into a cold reactor and subsequently heated to the desired reaction temperature.

The kinetic data, including rate constants, correlation coefficients and rate change time for the PW-1 tests are given in Table 5.2.

The calculated correlation coefficients indicated that the assumed kinetic model, viz. two first order reactions in series, is adequate for discussion purposes.

The COD content is directly proportional to heating value (approximately 13.9 MJ/kg) and, therefore, its destruction can be used as a relatively accurate measure of the quantity of heat potentially recoverable from a Wetox system. In this energy recovery application, it is important to maximize COD destroyed in the process, while minimizing temperatures, pressures and reactor residence time. From Figure 5.1 and Table 5.2, it is apparent that much of the overall COD destruction has occurred by the time of rate change. The values for COD destroyed at the inflection point versus the destruction realized at 30 minutes are compared in the following:

Temp. (°C)	Time of Rate Change (min)	COD Reduction (%)		% Reduction @ Rate Change / % Reduction @ 30 mins x 100 (%)
		@ Rate Change	@ 30 mins	
240	20.0	44.3	47.5	93
260	9.5	54.7	71.1	77
280	9.0	66.8	74.6	90
290	12.5	76.7	79.7	96

Thus, with the exception of the 260°C run, at least 90% of the starting COD is destroyed during the first reaction regime. The overall COD reduction ranged from 47.5 to 79.7%.

Referring back to Table 5.2, it can be seen that the rate constants calculated for the injected runs were consistently greater than those for the non-injected runs. Heating the batch reactor from ambient to the desired reaction temperature takes between 30 and 60 minutes, depending on the desired temperature. During this time, complex organics, such as bitumen in the produced water, are subjected to both oxidation and hydrolysis reactions. These reactions result in solubilization of macromolecules and partial oxidation to refractory species such as organic acids. The net effect is a retardation of the apparent reaction rate. Injections were conducted where possible, since this method more closely resembles the state of the organic entering a commercial continuous wet oxidation reactor.

The temperature dependence of the wet oxidation reaction rate constant was evaluated using the Arrhenius relationship.

The first reaction regime fitted the model and is shown in Figure 5.2 for both the injected and non-injected cases. The second reaction showed no such correlation with temperature, and, therefore, was not modelled using the Arrhenius relation. The non-conformity of the second regime to the Arrhenius equation is common. Small changes in organic concentration with time are probably insufficient to be measured accurately using the COD analysis.

Although some deviation from linearity may be expected in an Arrhenius relationship, a definite inflection point was observed (Figure 5.2). The exact point of inflection could not be inferred, due to the lack of quality data below 240°C. This characteristic is an indication that the produced water oxidation reaction is complex, having at least two predominant simultaneous reactions, each with its own activation energy. At low temperatures, (e.g. below 260°C), the reaction may be chemically controlled, whereas a physical limitation exists in the higher temperature range. However, this contradicts the belief that solid surface reactions preferentially occur during wet oxidation. This is discussed further in Section 5.1.4.

Table 5.3 presents the Arrhenius parameters for each set of reactions for the injected and non-injected cases.

(ii) Effect of Catalyst + pH Adjustment

Metal salts and low pH values have been shown to enhance the rate of chemical reaction in wet oxidation. These were examined in this programme, and compared to the reaction kinetics developed using produced water with no additives.

Copper salt was added to the produced water at a concentration of 200 mg/L (as copper) and runs were undertaken at temperatures of 220, 240 and 260°C. Similarly, H_2SO_4 was added to decrease the pH to 2 and tests were conducted at 220, 240 and 260°C. The effect of these additions are compared graphically for the 260°C run in Figure 5.3. Reaction rate constants, rate change times and COD reductions are tabulated in Table 5.4.

A significant rate enhancement was evident. At 260°C, for example, the rate constant increased by a factor of 2.2 and 1.6 with copper and acid addition respectively, as compared to similar tests with no additions.

The sensitivity of temperature change on tests with either copper or low pH are compared to the 'no addition' tests in the Arrhenius plot in Figure 5.4. Tests were not carried out beyond 260°C, and, therefore, an inflection point, as detected previously, was not observed. The Arrhenius parameters for the three conditions, viz no additions, 200 mg/L copper catalyst and acidified produced water, are tabulated in Table 5.5.

Considerable variation in the activation energy is evident between the three conditions. The low pH runs yielded the lowest values compared to the highest being recorded from the experiments with no additions. It is interesting to note that the produced water (no additions) at temperatures greater than 260°C had an activation energy very similar to that determined for either of the modified produced waters.

Although either the copper or acid addition enhances the oxidation reaction, and, thus reduces the operating duty (e.g. temperature, pressure, residence time) for the Wetox process, a cost benefit analysis will determine whether this is a desirable complication to consider.

5.1.2.2 Other Produced Water Tests

Three other produced water samples were examined in Ontario Research Foundation's batch wet oxidation unit. Two were from the Athabasca deposit, courtesy of Texaco Canada Inc., and the other was from the Esso Canada Ltd. Cold Lake pilot plant. All samples were received in 200 L drums. Although each was originally oil:water or water:oil emulsion, they had broken into two phases during transport: a heavy bitumen and water fraction. Only the aqueous fraction of these samples was used for testing.

Due to the dilute nature of these samples, injection into the 2 L batch system was not practical. Instead, therefore, all tests were conducted by pouring the sample directly into the open reactor, then sealing it, followed by heating to the desired temperature. The time at which reaction temperature was reached was referred to as t = 0.

Test conditions for all the experiments are given in Appendix D. Runs were conducted at temperatures from 240 to 280^{o}C and a selected few were done using copper catalyst and pH adjustment. An Arrhenius plot was constructed for the three different produced waters and is presented in Figure 5.5. Calculated activation energies and frequency factors are shown in Table 5.6.

Considerable variation between the three different samples is noted. The CLPW had an activation energy almost 5 times greater than that for the HTS sample. However, the value recorded for PW-1 (23,663 cal/mole) compared very closely with the CLPW. Evidently, mass transfer is strongly limiting in the HTS produced water. A possible reason for the disparity may be the concentration of bitumen in the different samples. The mechanism for the combustion of the soluble, or aqueous phase, would be expected to be quite different from the bitumen phase. In order to assess the bitumen reaction characteristics, attempts were made to wet oxidize the raw bitumen. Handling difficulties precluded getting dependable data at temperatures below about 280^{o}C. One test at 280^{o}C, however, did yield acceptable data using Cold Lake bitumen. The reaction rate constant was calculated to be 0.053 min^{-1} compared with 0.091 min^{-1} for the CLPW aqueous phase at 280^{o}C. Unfortunately, this one test cannot describe the reaction mechanism for raw bitumen alone.

(i) HTS Effect of Catalyst

Three experiments were performed to assess catalytic effects using copper at temperatures of 240, 260 and 280°C. The Arrhenius parameters determined for the initial reaction regime were:

Activation Energy	=	4492 cal/mole
Frequency Factor	=	4.2 min^{-1}
Correlation coefficient	=	0.964

The activation energy calculated for this case was slightly less than that determined under similar conditions with no catalyst addition (5248 cal/mole). It is apparent that mass transfer still dominates the mechanism of the reaction, and copper catalyst would have little noticeable influence on this controlling factor.

(ii) HTS - Effect of Oxygen Partial Pressure

A critical parameter in the design and economics of wet oxidation systems is the total pressure necessary in the reactor and heat exchanger components.

In most applications, it is desirable to minimize system pressure to reduce capital as well as energy costs for pumping and oxidant compression. The pressure is determined as the sum of liquid vapour pressure at the operating temperature, plus the oxygen partial pressure required for the reaction to proceed at reasonable rates.

In the many years of experience working with the Wetox process at Ontario Research, the reaction rates of very few organic materials have been shown to be dramatically affected by oxygen partial pressure.

Therefore, equipment is generally designed on the basis of steam vapour pressure at temperature, and overpressure evaluated on the basis of system mass and energy balances.

The produced water tests were conducted at a partial pressure of about 1.7 MPa (250 psi). A few runs were performed at 260°C, at overpressures deviating from the base case to determine if any pressure effects are apparent. Oxygen partial pressure was varied from 0.6 to 3 MPa. The initial reaction rate constant was not affected at partial pressures of about 0.9 MPa and greater. At a pressure of 0.6 MPa, the rate constant was reduced by about 33%, from 0.03 to 0.02 min^{-1}.

5.1.3 Produced Water Continuous Flow Tests

5.1.3.1 Single Compartment Test Unit

One test on Athabasca HTS produced water was undertaken in the small, 5 L, continuous flow reactor system which is described in Appendix B.

The test conditions for this one run were as follows:

- Temperature = 232°C
- Pressure = 4.3 MPa (625 psi)
- Copper Catalyst = 200 mg/L
- Residence Time = approx. 13 minutes

Oil and grease and COD analyses were performed on the feed, and the liquid (LPE) and vapour (VPE) phase effluents. These results and mass balances for the test are given in Table 5.7. The COD destruction realized was 42.1%, which compares well with that obtained during batch scale testing at similar conditions (after extrapolation to continuous flow operation). The oil and grease destruction was much greater, however, being just over 76%. It is apparent that the oil and grease contained in the feed were more readily destroyed during reaction through both hydrolysis and partial oxidation reaction.

5.1.3.2 Four Compartment Pilot Plant

Two tests were conducted using Athabasca HTS produced water in Ontario Research's 4 compartment, 50 L continuous flow pilot plant. A description of the operation of this unit is given in Appendix C.

The process conditions for the first trial are given in Table 5.8. Although the run appeared to be quite successful, examination of the test results showed poor mass balances with regard to oxygen consumption and COD reduction. The results are presented in Table 5.9. It can be seen from this table that the overall COD reduction is about 1.7 times greater than the oxygen consumed (3399/2000). This is unacceptable, since a 1:1 COD destroyed:oxygen utilization ratio is expected.

The second run was similar to the first, except no copper catalyst was added. The process conditions are given in Table 5.10. At the completion of this run, the pump outlet connection to the system heat exchanger was dismantled. A considerable quantity of tar was found built up and coating the walls of the piping. Because of this, therefore, no analyses were performed on Run #2. Furthermore, this may also explain the poor mass balances realized during the first trial.

5.1.4 Discussion

Although considerable handling problems were encountered with the produced water, experimental data generally correlated well. In many cases, runs were repeated, and, depending on the linear regression correlation coefficient, actual data from the original run were either discarded, or averaged with the new results. The assumption of two first order reactions in series as a reaction mechanism is believed adequate for discussion purposes and comparison of the experimental results. It is realized that the oxidation of an extremely complex organic such as bitumen comprises a multitude of reactions, and at many different orders of reaction.

Perhaps the most interesting development during the study of the kinetic mechanism of the produced water was the temperature dependence of the reaction. An inflection point, at approximately 240 to 260^{o}C, was observed in the Arrhenius relationship for PW-1 with no additions (Figure 5.2). Experiments were repeated over the temperature range to confirm the relationship, with the same effect. Evidently, at temperatures above the inflection point, the reaction is even more mass transfer limited than at the lower temperatures. However, this contradicts current thought that mass transfer is inhibiting at lower temperatures. The reason for this apparent anomaly is not well understood.

Either acid or copper catalyst addition would have the effect of reducing the activation energy of the wet oxidation reaction. Over the temperature range of less than 260^{o}C, this was, indeed, found to be the case. It was also observed that the calculated activation energies were quite similar to that calculated for PW-1 with no additive, at temperatures beyond the inflection point. This was particularly true for pH adjustment. This could suggest that a minimum activation energy (e.g. for a group of similar reactions) has been attained for the reaction, which does not become apparent except at high temperatures or with catalysts/pH adjustment.

Arrhenius parameters were found to be quite different between each of the produced waters tested. This was not unexpected, however, because organic material (e.g. bitumen) is extremely complex. Compounding this problem are physical differences such as concentration of free bitumen contained in the different samples.

In any case, a wet oxidation system applied in an oil field would receive produced water with characteristics far more variable than encountered in this study. Based on the experimental results, therefore, more consistent and reliable operation would be expected at temperatures of greater than 260°C.

5.2 Coke Wet Oxidation Experiments

Bitumen recovered from Alberta's oil sands has to be subjected to one of a variety of primary upgrading processes prior to being acceptable, and pumpable, to existing refineries. There are essentially two system types available to achieve these goals - carbon rejection or hydrogen addition.

Syncrude Canada Ltd. and Suncor Canada Ltd., Fort McMurray, Alberta, both employ carbon rejection type processes in their oil sand mining complexes. Syncrude employs a continuous process, called fluid coking, whereas Suncor uses a batch type called delayed coking. At the elevated temperatures of both processes, a variety of reactions occur resulting in all of the feedstock being converted to vapours and by-product coke. Most of the sulfur and virtually all the metals are deposited along with the coke. Although the cokes have a high heating value, their use for combustion is limited due to high sulfur dioxide emissions and ash contents.

The coke by-product from the fluid coking process is about 10% of feed bitumen, and about 20-25% in the delayed coking process(2,3). Some of these by-products are currently burned for on-site energy production, but a considerable amount is stockpiled at the two oil sand mining facilities.

One of the original objective of this research programme pertaining to coke wet oxidative treatment, was to preferentially oxidize the sulfur in the coke. Thereafter, the low sulfur coke could be incinerated in conventional equipment eliminating the need for extensive flue gas desulfurization. This concept has been proven feasible on coal in earlier development work at Ontario Research. By operating the Wetox process at low temperatures and pressures, coal desulfurization efficiencies have been recorded in the order of 75%, with minimal loss of the coal carbon(4).

5.2.1 Description of Cokes

Samples of both a fluid and delayed coke were obtained for testing. Sufficient fluid coke was collected for pilot scale experiments, and only small quantities of delayed coke for batch testing were obtained.

Heating values, and proximate and ultimate analyses were performed on the delayed coke samples. These are given in Table 5.11. In addition, sulfur analyses were conducted on the fluid coke, the results of which were (General Testing Laboratories, Toronto):

Leco:	2.73%
Bomb:	2.88%

Difficulties were experienced in rationalizing the mass balance for sulfur in the wet oxidation reaction, based on the reported sulfur analyses. Specifically, at the more severe batch Wetox operating conditions, more sulfur (as soluble sulfate) was found than could be accounted for on the basis of supplied coke sulfur. Ontario Research's ion chromatographic instrument was rigorously checked, as were potential sources of contamination in the experimental and analytical laboratories. No problem areas were found, and, therefore, the initial coke sulfur analyses were suspected to be low. According to the Alberta Oil Sands Sample Bank, who frequently deal with Alberta petroleum cokes, the typical sulfur content of Suncor delayed coke is 6-6.5%, and the Syncrude fluid coke sulfur concentrations range from 6-9%(22).

For the purposes of this experimental program, it was assumed that the sulfate analyzed in wet oxidized solutions, at the most severe reaction condition, is an indication of the sulfur content of the feed coke. This assumption is believed valid because, at the end of these high temperature reactions, essentially all (e.g. greater than 95%) of the coke has been oxidized, and, therefore, the sulfur will be measured in solution as sulfate. From a number of experiments, the delayed coke sulfur content was calculated to range from 5.9 to 6.8% with an average of 6.3%. With the exception of one anomalous result, the fluid coke sulfur content was determined to be 7.5 to 7.7% with an average of 7.6%.

5.2.2 Fluid and Delayed Cokes - Batch Testing

The range of wet oxidation reaction conditions studied for fluid and delayed cokes was:

- Temperature: 220° to 320°C
- Pressure: 3.8 to 10.3 MPa (550 to 1500 psi)
- Residence Time: up to 150 minutes
- Additions:
    - sodium hydroxide
    - sulfuric acid
    - copper oxide catalyst
    - surfactant (sodium alkylaryl sulfonate)
- Mesh Sizes
    - -250 (referred to as 250 mesh)
    - +250 -100 (referred to as 100 mesh)
    - +100 -60 (referred to as 60 mesh)

COD or SS (suspended solids) analyses were used to follow the course of the wet oxidation reaction. Sulfate (measured by ion chromatography) was performed on selected samples to determine coke sulfur oxidation kinetics.

5.2.3 Delayed Coke Test Results

(i) No Additions

The major objective of these experiments was originally to effect desulfurization of the delayed coke in the Wetox process. As the sulfur to sulfate oxidation reaction was anticipated to be substantially greater at less severe reaction conditions than the actual rate of the carbon conversion reaction, low carbon losses were predicted. A number of preliminary experiments indicated that this concept was not practical. Instead, the sulfur and carbon oxidation rates were found to be similar at basically all temperatures investigated.

The sulfur oxidation was compared to the carbon (as measured by COD) assuming first order reaction kinetics. This comparison is given in Figures 5.6, 5.7, and 5.8, for 240, 260 and 280°C respectively. Potential sulfate remaining, indicated on the ordinate, was calculated to allow a direct comparison between the rates of carbon and sulfur oxidation. Basically, it is defined as the weight of sulfur remaining in the coke at a particular reaction time, which, theoretically, could all be oxidized to sulfate.

The carbon and sulfur first order reaction rate constants for the three test cases are presented in Table 5.12. The similarity between the rate of desulfurization and that of carbon oxidation is apparent. These comparisons were made at a residence time of 60 minutes or less. At extended reaction residence times, it was found that sulfur conversion was essentially 100%. At similar times, the carbon (as measured by COD or SS analyses), plateaued at somewhat greater than 90% reduction. This is due to soluble refractory organics being measured by the COD analysis, or ash, which contributes to a SS content.

Based on the results of this study on the relative rates of sulfur and carbon oxidation, it was clear that the original desulfurization concept was not feasible. At this juncture, emphasis was shifted to maximize the carbon oxidation reaction, and, hence, energy production, from within the Wetox process itself.

Test conditions for the many experiments are given in Appendix D. Three different mesh sizes were tested, with the baseline or fundamental analyses being developed using 100 mesh size material. Experiments were undertaken at temperatures from 200 to 320°C, with and without catalysts and pH adjusting additives. Reaction kinetics were monitored using COD or SS analyses. Data were fitted to assume two first order reactions in series, and rate constants and correlation coefficients were calculated. Plots yielding correlations poorer than 0.95 (for the first reaction regime) were repeated. Experimental results at a temperature of 200°C could not meet this criterion, and, therefore, were not included in the kinetic analysis.

Coke is not a complex organic material relative to the produced water. Carbon comprises the bulk of the material, and, as such, its combustion characteristics appear simple. In the wet oxidation of many organic substrates, it is found that the inflection point between the first and second reaction regimes occurs after about 40-75% of the organic carbon measured by COD has been oxidized. Using produced water (PW-1 at 260°C) as a typical example, it was found that 55% of the influent COD was destroyed had occurred during the first reaction.

However, with coke, the first reaction regime is prolonged, and beyond the inflection point, essentially no combustion occurs. This characteristic is shown in Figure 5.9 for two temperatures. Kinetic data and COD reduction efficiencies are given in Table 5.13 at all temperatures for 100 mesh, delayed coke without additions.

At the lower temperature (e.g. 240°C in Figure 5.9), a second reaction regime was not observed even after 150 minutes of reaction. By comparison, at 290°C, an inflection point is noted at approximately 60 minutes. As the temperature is increased over the range studied, a decreasing time to rate change is noted. At virtually all temperatures studied, the COD reduction at the rate change is almost equivalent to the COD reduction attained at the termination of reaction, which corresponds to essentially 90-95%. One anomaly is seen at 280°C in Table 5.13, where 98% reduction is seen at the rate change, which increases to 99% at 150 minutes.

(ii) Effect of Mesh Size

The baseline data for delayed coke was generated using 100 mesh size material. A limited number of tests were conducted using a 60 mesh and 250 mesh size. The objective was to provide some insight into the mechanism which controls the rate of reaction.

Conditions for these experiments are presented in Appendix D. Reaction rate constants were calculated, and are compared to the 100 mesh constants in the Arrhenius relationship given in Figure 5.10. Activation energies and frequency factors follow in Table 5.14.

The 60 mesh coke experiments yielded an activation energy greater than that of the two smaller particle size test series. One would expect the opposite, because, with larger particle size, the reaction should become less sensitive to temperature change. Difficulty was experienced in obtaining acceptable samples during the 60 mesh run, and, therefore, tests were done without sampling (at 240 and 260°C). For these tests only, the loaded reactor was heated to temperature, operated for each of 30, 90 and 150 minutes, and samples were withdrawn from the cooled, depressurized reactor. This difference in test procedure may be an explanation for the questionable trends observed in Figure 5.10.

(iii) Effect of Catalyst

The effect of copper catalyst addition on the delayed coke reaction kinetics was studied at three temperatures: 240, 260 and 300°C. Experimental conditions are presented in Appendix D. The Arrhenius parameters calculated for the reaction are given below:

Activation Energy:	11,840 cal/mole
Frequency Factor:	3,500 min^{-1}
Correlation:	approximately 1

The activation energy is approximately 25% less than that calculated for the delayed coke without additions. At temperatures greater than about 280°C, little benefit is gained by the use of copper catalyst, whereas, at 240°C for example, an approximately two-fold increase in rate is apparent.

These trials were conducted using a 200 mg/L copper concentration. Increasing the concentration to 320 mg/L at 240°C had no noticeable effect on the reaction rate, while a 25% reduction in rate was noted after decreasing the copper concentration to 80 mg/L.

It was found that the fluid coke oxidation reaction (see Section 5.2.4) consisted of a characteristic induction period, followed by the "typical" first order kinetic reaction. An anionic surfactant, sodium alkyl aryl sulfonate, was shown to virtually eliminate this period. Although no induction period was observed during the delayed coke reaction, it was of interest to determine if this additive affected the rate of reaction. One test was done at 260°C, using 50 mg/L sodium alkyl aryl sulfonate. A marginal improvement in rate was achieved, increasing from 0.028 to 0.034 min^{-1}.

(iv) Effect of pH Adjustment

The influence of both high and low pHs on the sulfur and carbon oxidation reactions was studied. Low pHs are known to enhance the rate of most wet oxidation reactions, probably due to an increase in generation of free radicals. Conversely, higher pHs frequently have the effect of suppressing the carbon reaction rate. Caustic addition has also been shown in previous work to enhance desulfurization of inorganic sulfur from coal. The test data for these experiments are given in Appendix D and representative results are presented here.

The investigation into the effect of pH proved interesting. It appears that both high and low pHs suppressed the carbon oxidation reaction. Elevated pHs also slowed the sulfur to sulfate reaction. Sulfur oxidation was not measured at reduced pHs because sulfur was monitored in solution as sulfate, and sulfuric acid is employed to acidify the solution.

The dramatic effect of sodium hydroxide concentration on the rate constant is shown in Figure 5.11 for a representative set of trials conducted at 260°C.

It is likely that the additives (sulfuric acid, sodium hydroxide) acted as negative catalysts, or inhibitors. A comparison of the Arrhenius parameters determined at the various conditions is given in the following:

Condition	Frequency Factors (min^{-1})	Activation Energy (cal/mole)	Correlation Coefficient
No addition	44,103	15,167	0.993
H_2SO_4 to pH = 2	33,556	15,538	0.995
0.1 g/L NaOH	6.34×10^6	21,620	~ 1
3 g/L NaOH	7.7×10^{12}	37,202	1.0*

*Rate constants calculated using only 2 data points. The correlation coefficient calculated for the low temperature run was less than 0.95, and, therefore, was not included.

From the above comparison, it is apparent that the activation energy at either lower or higher pHs is greater than the base case condition. Furthermore, as the NaOH concentration increases, a corresponding increase in activation energy is observed.

The preceding gives an indication that pH may be a significant factor in the wet oxidation of coke reaction. It is not possible, however, to do a realistic assessment of the impact of pH on a batch scale. The 2 L batch unit employed for most of the tests has a limitation on the total pressure, and, hence, the amount of oxygen which can be supplied. Ultimately, this limits the allowable coke concentration to a practical test concentration of 3 g/L, which is at least an order of magnitude less than that anticipated for full or pilot scale operation. As the reaction proceeds, sulfuric acid is produced from the coke sulfur. Obviously, the higher the feed coke concentration, the greater the sulfuric acid concentration generated. It could be inferred, therefore, that the specific rate of the reaction would tend to diminish as the reaction progressed.

To give a little more insight into this phenomenon, two tests were conducted at 9 g/L coke or three times the base case coke concentration at 260°C. One test was done with no other addition, and the other was conducted with 0.5 g/L sodium hydroxide, which is approximately one third that stochiometrically required for neutralization of the produced acids. The reaction rates calculated for both of these runs were greater than that calculated for the 3 g/L test. Specifically, the rate constants were:

9 g/L delayed coke (no addition)	K	=	0.046 min^{-1}
9 g/L delayed coke (0.5 g/L NaOH)	K	=	0.052 min^{-1}
3 g/L delayed coke (no addition)	K	=	0.03 min^{-1}

Based on these quite preliminary results, it is still difficult to rigorously assess the effect of pH (similar behaviour was also observed with fluid coke, Section 5.2.4). This matter will be discussed further in Section 5.2.5.

(v) Effect of Oxygen Partial Pressure

The base case data for delayed coke were generated at an oxygen partial pressure of about 1.7 MPa. Three tests were performed at 260°C, at overpressures deviating from this case to establish necessary reaction oxygen pressures. A plot of specific reaction rate constant versus oxygen partial pressure is presented in Figure 5.12. The effect is evident, with a slowing of rate change being observed at about 1.7 - 2 MPa.

5.2.4 Fluid Coke

The sulfur and carbon wet oxidation characteristics of delayed coke were investigated in the programme. However, since it was found that coke desulfurization is not a practical treatment option, the sulfur oxidation kinetics were not studied in detail in the case of the fluid coke. Instead, therefore, emphasis was placed on "total" combustion for energy recovery from the Wetox process itself.

The baseline reaction kinetics were developed using 100 mesh coke, and comparisons of 60 and 250 mesh size were conducted thereafter. Again, as described for the delayed coke and produced water experiments, all test results were examined assuming first order kinetics. Linear regression was employed and those test runs exhibiting a correlation coefficient of less than 0.95 were repeated. In some cases, test results from runs were averaged, providing the minimum acceptable correlation coefficient was met.

(i) No Additions

The oxidation characteristics of the fluid coke were found to be markedly different from those determined for the delayed coke. Plots of logarithmic COD remaining versus reaction time at 240, 260 and 280^{o}C are given in Figure 5.13, followed by 300 and 320^{o}C in Figure 5.14. At the lower temperatures, a distinct initiation or induction period is apparent. This time varies from essentially 0 minutes at 300 and 320^{o}C, to approximately 60 minutes at 240 to 260^{o}C. The nature of the reactions beyond the initiation time are similar to those described previously for the delayed coke, except that rate for fluid coke is approximately 50% lower. At 240 and 260^{o}C, only one reaction was observed. As the temperature is increased, two reactions become apparent, being most pronounced at the highest temperature studied, 320^{o}C. This behaviour (e.g. lack of two rates at low temperatures) is probably due to insufficient residence time being allowed during the lower temperature tests. In other words, it is suspected that an inflection point would be seen at virtually all temperatures, with the time to rate change increasing with decreasing temperature. Furthermore, regardless of reaction temperature, a COD reduction, or combustion efficiency of greater than 90% would be attained.

A summary of the reaction rates and correlation coefficients for the five temperature conditions are given in Table 5.15. For those experiments exhibiting an initiation time, those parameters are calculated beyond this time.

Two methods were examined in an attempt to reduce, or eliminate, the observed induction period:

1. The Wetox reactor was operated at lower temperatures (e.g. 100 to 220^{o}C) for 60 to 90 minutes, with oxygen, and then the temperature was raised to that desired (i.e. simulation of a two stage, wet oxidation system). The reasoning for this methodology is that diffusion is not a strong function of temperature. Therefore, the mass transfer barriers may be penetrated if sufficient residence time is allowed.

2. A surfactant (sodium alkyl aryl sulfonate) was added to enhance mass transfer at the particle boundary.

Both methods were effective and essentially yielded reaction rates similar to those determined beyond the initiation period. A comparison of the preheat test (90 minutes at 220^{o}C), the surfactant addition, and the "normal" condition is shown graphically in Figure 5.15 for the 260^{o}C test case. Both of the system perturbations tended to simply shift the curve to the left. The specific reaction rates varied from only about 0.02 to 0.023 min^{-1}, suggesting that the only effect was, in fact, to reduce the mass transfer limitation causing the initiation period.

Adding a small concentration of surfactant to the feed slurry is simpler and probably the more attractive of the two alternatives. Thus, for the remainder of the tests on fluid coke, this additive was employed.

(ii) Effect of Particle Size

A number of tests were conducted using a 60 mesh and 250 mesh size fluid coke. Due to the size of the sampling ports on the batch Wetox reactor, the data for the 60 mesh did not correlate as well as the smaller particle size. This resulted in many repeat runs being necessary. Going to a larger particle size than 60 mesh, therefore, was not considered practical in the present equipment.

Test conditions are described in Appendix D. The most important evaluation of the effect of particle size is its influence on the Arrhenius parameters, in particular, the activation energy. The Arrhenius relationship for the three different mesh size cokes is presented in Figure 5.16 A comparison of the activation energies, frequency factors and correlation coefficients is tabulated in Table 5.16.

As was expected, the activation energy increases with a decrease in coke particle size. This infers that mass transfer contributes to the control mechanism of the oxidation reaction. However, based on the absolute values of the activation energies, it is suspected that both temperature change (i.e. chemical reaction) and mass transfer influence the reaction rate.

(iii) Effect of Copper Catalysts

Heavy metal catalysts, most notably copper, are known to increase the reaction rate of many wet oxidation reactions. This addition was investigated on fluid coke in the 240 to 280^{o}C temperature range for both 60 and 100 mesh sizes. Test data are given in Appendix D.

The Arrhenius parameters for coke oxidation using copper catalyst are presented below:

Activation Energy:	17,030 cal/mole
Frequency Factor:	2.86×10^5
Correlation:	0.993

Very little difference was found between the activation energy above and that calculated for the fluid coke, 100 mesh, no addition. A significant increase in the magnitude of the frequency factor for the catalyzed range is apparent, however, which effectively suggests a rate enhancement over the temperature range studied ranging from about 50 to 100%.

(iv) Effect of pH

As was discussed in Section 5.2.3 on delayed coke, it is not possible to undertake a rigorous analysis of pH effects in a batch scale system. As a consequence, it was decided not to alter the pH downwards using sulfuric acid. Two runs were performed using 9 g/L fluid coke, similar to those tests using delayed coke. A comparison of the reaction rate constants calculated from these two tests are compared to the 3 g/L trial.

Condition	Rate Constant (min^{-1})
260°C, 3 g/L, surfactant only	0.02
260°C, 9 g/L, surfactant only	0.03
260°C, 9 g/L, surfactant + 0.5 g/L NaOH	0.0295

The rate constant for the 9 g/L runs (with or without caustic addition) was 50% greater than the 3 g/L base case trial. Whether that is due to downward pH or to an increase in heavy metals which, possibly, may be catalyzing the reactor is unknown. In any case, the actual effect of pH must be analyzed on a pilot scale, in which coke concentrations could be increased to practical operating levels.

(v) Effect of Oxygen Partial Pressure

The fluid coke wet oxidation reaction, like delayed coke, was found to be significantly affected by changes in oxygen partial pressure. Experiments were conducted at incremental oxygen partial pressures above vapour pressure, ranging from about 0.38 to 3.46 MPa. The experimental conditions are given in Appendix D. A plot of reaction rate constant versus oxygen overpressure is presented in Figure 5.17. These tests were performed at 250°C, using copper catalyst addition.

The pressure influence is apparent. Reaction rate increases dramatically to about 1.5-1.7 MPa, beyond which a plateau is observed. This flat portion of the curve corresponds to a rate constant of about 0.038 min^{-1}.

5.2.5 Fluid Coke Pilot Plant Testing

Six runs were conducted in the Ontario Research 4 compartment continuous flow Wetox pilot plant (see Appendix C for a description of the unit). All of the attempts resulted in extremely poor mass balances of oxygen utilization versus coke oxidation. As a result, therefore, no dependable quantitative data were obtained from the extensive test program. A complete description of the trials, including conditions, results, problems and solutions is given in Appendix E.

5.2.6 Discussion of Fluid and Delayed Cokes

Chemical leaching or desulfurization of petroleum cokes from western Canadian oil sands was demonstrated to be impractical during the experimental program. In essence, the sulfur contained in the coke oxidizes at a similar rate to the carbon itself. This is probably due to the fact that the sulfur is primarily organic, rigidly bound to the carbon structure. The reaction occurs at the surface of the particle, where the carbon and sulfur compounds react simultaneously. Theoretically, this heterogeneous reaction type is common, and can be described mathematically by the "unreacted core" model(5).

Although the foregoing suggests that mass transfer is controlling the rate of reaction, particle size tests did not definitively prove this to be the case. Increasing the surface area available for reaction (e.g. decreasing the particle size) did reduce the system activation energy, but likely less than that which would be expected in a substantial mass transfer or diffusion control reaction. Unfortunately, the present batch equipment employed for testing did not permit large particle sizes to be examined. In addition, grinding the coke to 250 mesh took considerable effort, and, therefore, smaller particle sizes above this value were deemed impractical.

As minimal grinding is desirable for full scale operation, pilot testing may confirm whether larger particle sizes could be fed to the Wetox process. On the basis of available data, a 60 mesh size feedstock appears to be feasible.

The wet oxidation of coke reaction is quite different as compared to most other organic materials. A prolonged first reaction regime was observed in all coke testing. Regardless of reaction temperature, this regime continues until 90 to 95% coke destruction is realized. Obviously, this is an important benefit of the Wetox process applied to combustion of fuels for energy recovery in oil sands operations.

The reason for this behaviour is attributable to the non-complex nature of coke. Basically, the coke is comprised largely of carbon, with small concentrations of hydrogen, sulfur and metals. As a consequence, most of the coke is converted to carbon dioxide, water, sulfuric acid, etc., with little concommitant production of refractory by-products whose oxidation forms the much slower second reaction regime.

A definite initiation time was observed on the lower temperature tests using fluid coke. This time was virtually eliminated by adding low concentrations of an anionic surfactant to the starting liquid. The role of the surfactant is probably a combination of the following:

1. It reduces the surface tension of the liquid at the particulate interface, and,
2. It can electrically charge the bubble surface, thereby producing ionic air bubbles, which tend to retard coalescence, and, hence, increase the interfacial area for mass transfer(6).

This additive is effective at temperatures below about 260°C. At higher temperatures, any effect is virtually unnoticeable due to the decreased initiation time under normal operating conditions.

Oxygen partial pressure was found to have a significant impact on the oxidation of delayed or fluid coke reaction. A system designed for coke treatment must incorporate an overpressure, above steam pressure, of at least 1.7 MPa. If an air (as opposed to oxygen) system is desired, the required overpressure is approximately 7.3 MPa.

pH was also found to have an influence on the oxidation reaction. It is impossible, however, to identify the magnitude of the effect of pH on a batch scale. Acidification of the solution at the start of reaction evidently retards the reaction rate. When the starting coke concentration in the test unit was increased by a factor of three (resulting, therefore, in a threefold increase in sulfuric acid production during reaction), an actual enhancement of rate was observed.

A possible reason for this apparent anomaly is presented in the following, based on the assumption that metals contained in the coke, upon solubilization, catalyze subsequent oxidation.

Under normal pH (e.g. neutral) initial condition, the oxidation reaction proceeds uninhibited. As the particle is being oxidized, metals (e.g. iron, vanadium, etc.) are solubilized and appear in solution as homogeneous catalysts, which consequently enhance the rate of reaction. Obviously, increasing the starting coke concentration, increases the catalyst concentration, which enhances the rate of reaction. The nature of these catalysts is not known. In the case of an artificially acidified starting solution, a pH inhibition may be evident. This results in the reaction proceeding more slowly, and, therefore, a reduction in the rate of homogeneous catalyst production.

The validity of the preceding argument cannot be verified. Only pilot scale testing, using equipment designed for coke wet oxidative treatment, can give insight into the effect of higher coke concentrations.

Although the pilot scale testing in the present research program provided no dependable kinetic information on the continuous flow treatment of coke, a number of important practical conclusions were derived:

- A unit capable of handling higher temperatures and pressures is required.

- Careful consideration must be given to using pitched blade impellers on the agitators. On a pilot unit, impellers must be made removable for easy examination of different pitch angles, etc.

- Feed tanks must be efficiently agitated.
- Feed line constrictions should be eliminated.
- Heat exchange systems for feed preheating must be minimized, or eliminated.
- Feed lines should slope down to the reaction vessel.
- A portion of the total oxidant flow should be injected into the feed line to promote turbulence, and minimize coke precipitation.
- High velocities (e.g. 2-3 m/sec) should be maintained in any coke slurry lines

5.3 Athabasca Pitch

Samples of Athabasca and Cold Lake bitumens were processed in the Eureka upgrading system for AOSTRA. After receiving the upgraded by-product, solid pitch, AOSTRA generously gave small samples to Ontario Research for wet oxidation testing. The Eureka process is a carbon rejection type which operates at lower temperatures than either fluid or delayed coking.

5.3.1 Description

The pitch sample was much more friable than the coke samples. Since Ontario Research only had quite small quantities of the material, ultimate, proximate and heating value analyses were not performed. Sulfur was analyzed, however, and its concentration was found to be 5.8%, using the Leco method.

5.3.2 Batch Test Results

Batch trials were conducted at temperatures from 220 to 320°C, with and without catalyst or pH adjustment. All samples were injected into the batch autoclave after the desired temperature was attained. Different mesh sizes were also investigated, but data generated using the 60 mesh size could not be correlated very well, and, therefore, are not included in the kinetic analysis.

Graphs of logarithmic COD remaining versus residence time are given in Figure 5.18 for 100 mesh size pitch with no additives, for trials conducted at temperatures from 220 to 280°C. The 320°C test data are presented in Figure 5.19. Corresponding kinetic data for all temperatures are tabulated in Table 5.17.

The characteristics of the pitch oxidation reaction are quite similar to those described for delayed and fluid cokes (less the initiation time). The first reaction regime is lengthy, and the second regime is not apparent until a temperature of about 260°C is attained. Again, regardless of reaction temperature, organic reductions at the time of rate change are expected to be approximately 90-95%. However, absolute specific reaction rate constants are considerably higher over the temperature range. The net result, therefore, is that the residence time required to realize 90-95% reduction is much less for pitch than either delayed or fluid coke. At 260°C, using 100 mesh material as an example, the time to rate change for pitch is approximately 55 minutes, at which time a COD reduction of approximately 90% is achieved. At similar conditions with delayed coke, the time to rate change is approximately 92 minutes, with a corresponding COD reduction of 90.3%.

Experimental conditions of trials with catalyst or pH adjustment, and using 250 mesh starting particle size are given in Appendix D. Reaction rate constants for these experiments were calculated and are compared to the base case condition in the Arrhenius plot given in Figure 5.20. Arrhenius parameters are presented in Table 5.18.

The absolute values of the activation energies probably indicate that mass transfer is not limiting the pitch oxidation reaction. Instead, the sensitivity of the reaction with temperature changes suggests a chemical reaction limitation. This is not surprising in view of the fact that the pitch is extremely porous, and, therefore, considerable surface area is available for reaction. The small variation of the activation energy between the 100 and 250 mesh size confirms this theory. Increasing the mesh size from 100 to 250 results in only about a 15% decrease in activation energy.

(ii) Effect of Oxygen Partial Pressure

The experiments undertaken on Athabasca pitch were done using an oxygen overpressure of approximately 1.7 MPa. Essentially no difference in system performance was seen at 1 MPa. However, operation as low as 0.2 MPa resulted in a reaction rate constant being over 8 times lower than that observed at higher pressures.

5.3.3 Discussion

The combustion characteristics of Eureka pitch were similar to those observed for the cokes. A long first reaction regime is evident, which proceeds until 90-95% reduction is realized. The major difference, however, is that reaction rates for pitch are greater over the temperature range studied, resulting in a shorter residence time to realize the desired performance as compared to coke.

5.4 Asphaltenes

Two Toronto entrepreneurs have invented an "at the wellhead" produced bitumen deasphalting process. Known as the Angelov-Shibley process, it is currently being marketed by Wade Engineering Ltd. of Toronto. The exact details of the process were not disclosed, but it is based on some type of pentane extraction technology.

A small pilot scale process is operated in Toronto, from which Ontario Research obtained a small (approximately 100 g) sample of the asphaltene by-product. The practicality of employing wet oxidation to combust this material, to generate steam for solvent recovery, was investigated on a batch scale.

5.4.1 Asphaltene Description

The asphaltenes were much softer than either the coke or the pitch samples. They were received damp, with quite a strong pentane odour. Insufficient material was obtained to perform detailed analyses. According to the inventors, however, the sulfur content is expected to be over 7%, and most of the metals contained in the feed bitumen would be deposited with the asphaltenes.

5.4.2 Asphaltene Test Results

A limited number of trials were conducted on this material at temperatures from 240 to 280^{o}C. The effect of copper catalyst was also evaluated.

In general, the experimental data were found to be quite reliable. Test conditions are provided in Appendix D. A plot of logarithmic COD versus residence time is presented in Figure 5.21 at one temperature (280°C) to compare reaction kinetics with and without copper catalyst.

The rate constant with no additions was determined to be about 0.032 min^{-1}. This figure compares reasonably well with the rate constant for fluid coke at the same temperature. However, copper catalyst enhances the rate by a factor of approximately 5.8 times. A considerable rate enhancement was also noted at 240 and 260°C with catalyst addition.

An Arrhenius plot was made and is given in Figure 5.22, followed by the critical parameters in Table 5.19.

The copper catalyst resulted in a very significant increase in both the activation energy and frequency factor for the reaction. The combustion with no additions appears to be quite mass transfer limited, but, with a catalyst, chemical reaction is probably the limiting factor.

5.4.3 Discussion

In many respects, the nature of the oxidation reaction for the asphaltenes was analogous to the solid fuels (e.g. coke and pitch) discussed previously. A long first order reaction was observed, and, by the time of rate change, approximately 80-90% oxidation was attained, or about 10-15% less than that observed for the delayed and fluid cokes.

A dramatic enhancement of rate and extent of reaction was noted for tests with copper catalyst. With no addition, the reaction was clearly mass transfer controlled. Catalyst increased the activation energy by about 2.6 times, from 6,612 to 17,585 cal/mole. This behaviour is somewhat contradictory to expectation, as catalysts in wet oxidation generally reduce the activation energy, and, therefore, become more effective with decreasing temperatures.

5.5 Mixed Coke/Produced Water

A limited number of experiments were performed on fluid or delayed coke mixed with a sample of produced water. The objective was to determine if any synergistic or antagonistic effects are apparent.

5.5.1 Description

The "HTS" produced water sample was used for these experiments. Fluid or delayed coke was added to the diluted produced water to realize, approximately, a one third COD contribution from the produced water and a two thirds coke COD contribution.

5.5.2 Results

The experimental data from these trials did not reproduce as well as those from tests using either coke or produced water alone. This was probably due to the fact that the powdered coke (100 mesh), which is preferentially oil wetted, would tend to break the otherwise stable oil:water emulsion. Therefore, at the start of the reaction, the bitumen would be separated from the aqueous phase, and would adhere to the internals of the reactor.

The temperature range investigated was 240 to 280^{o}C, with and without copper catalyst. Very poor correlation was determined for runs using delayed coke without catalyst, and, therefore, these data are not presented. Test conditions are listed in Appendix D.

The overall reaction characteristics for the mixed waste samples were, in appearance, similar to those described earlier for fluid and delayed cokes. In essence, a prolonged initial reaction regime was observed, proceeding until greater than 90% of the starting organic was destroyed. An example case is illustrated in Figure 5.23 for each of fluid and delayed coke with HTS produced water, and copper catalyst at 280°C.

The rate constants calculated for these two tests are presented in Table 5.20, along with those for the individual components. In addition, a rate constant was calculated for the mixed waste tests, based on the fractional contribution of the two components. In both cases, the calculated rate constant was significantly greater that the actual (approximately 76% for fluid/HTS + Cu; 43% for fluid/HTS; 32% for delayed/HTS). This indicates that some antagonistic effects are, indeed, apparent.

It was suspected that mass transfer would tend to suppress the activation energy of the reaction. As mentioned previously, the fine coke particles are preferentially oil wetted, and, therefore, may become encapsulated by a resistant oil film boundary layer. To evaluate this theory further, an Arrhenius plot was constructed using the reaction rates calculated for the different mixed waste test series. This is shown in Figure 5.24 and correlation coefficients in Table 5.21. Activation energies were again calculated, based on the contributions of the individual components to the overall waste.

Both catalyzed waste mixtures conformed to the aforementioned theory, whereas the uncatalyzed tests yielded an actual activation energy approximately 17% greater than that calculated.

5.5.3 Discussion

The COD contribution from each of the produced water and solid fuel phases was arbitrarily pegged at about 67% and 33% respectively. In an actual operating system, it is probable that the solid fuel contribution would be greater, perhaps in the order of 90% of the total feed organic to a Wetox process. By increasing the produced water component, however, more pronounced synergistic or antagonistic effects could be noted.

The reaction, overall, behaved much like the solid fuels reactions. A lengthy first regime occurs, during which approximately 90% reduction or greater is realized. Antagonistic effects were observed, however, probably due to an oil film creating a mass transfer limitation at the particle boundary.

5.6 Vapour Phase Catalysis

5.6.1 Introduction

It is widely recognized that acetic acid is the most refractory organic component in wet oxidation systems(7). Acetic acid also forms a large proportion of the volatile fatty acids (VFAs) which contribute to the residual organic loading of the vapour phase effluents (VPEs) of wet oxidized material. Formic acid, on the other hand, is more readily removed from these effluents. The oxidation of dilute aqueous streams of formic acid have been studied by Goto and Smith(8,9) using various catalysts in a pressurized trickle bed reactor at 200-240°C and 40 atm. For comparison, temperatures of 250-286°C were required to oxidize acetic acid under similar conditions(7).

The purpose of this section of the work was to develop a gas phase reactor system to remove VFAs from the vapour phase effluent of the Wetox system. Removal of the VFAs is necessary to render the effluents suitable for in-situ, high pressure steam injection. If injection steam were not needed, the catalysis system would simply provide an alternative to conventional biological or chemical oxidation processes for clean-up of the vapour phase condensate prior to discharge. A vapour phase reactor was, therefore, required in contrast to the work of Smith et al(7-9), who chose to work in the liquid phase. The mechanism of reaction at the catalyst surface in vapour phase reaction was not thought to be significantly different from that in the liquid phase. An upflow reactor design was chosen for three reasons:

(a) the incidence of channeling was thought to be reduced
(b) non-volatile leachates would remain in the catalyst bed
and (c) the potential for settling and plugging would be reduced.

5.6.2 Design and Construction of the Reactor

Having decided upon the basic reactor configuration (viz. vapour phase, pressurized, upflow, heterogeneous catalyst bed), it was necessary to provide high pressure feeds for contacting effluent and air at the catalyst surface. On the downstream side, a condenser system was required for analysis purposes, followed by a manually-operated let-down valve. The apparatus is illustrated schematically in Figure 5.25.

A metered liquid feed system was provided by linking a feed reservoir to a high pressure plunger pump and the liquid was vaporized and preheated electrically before mixing with high air pressure from a bottled supply. The air-feed mixture was then passed into the catalyst chamber which was externally heated to prevent condensation. The temperature of the reactor was above the critical temperature of the system and the pressure was maintained by a regulator attached to the air bottle. Air flow was monitored by regulation of the let-down control valve.

The reactor itself was a 2 L titanium autoclave with a flanged and sealed inlet port in its base.

Early work with a 1 litre catalyst bed was not satisfactory for laboratory experimental purposes since our electrical heating system was not sufficient to maintain the high vapour flows required to exceed the capacity of the catalyst. The maximum catalyst bed volume was, therefore, decreased by a factor of 10 to approximately 200 mL. This was achieved by fitting a stainless cylinder into the autoclave body. The cylinder was fitted with an inlet feed pipe at the bottom and the top was covered with approximately 70 mesh stainless steel sieve material to retain catalyst particles. The annular space was filled with sand as a heat transfer medium.

5.6.3 Results and Discussion

(i) Noble Metal Catalysis

Early work was carried out using a commercial platinum catalyst on a honeycomb alumina support. The catalyst was broken into small (1-2 cm) pieces and placed in the catalytic reactor. The density of the packing was approximately 0.5 g/cc. Aqueous acetic acid solutions were used as model solutions for process water, in these early studies.

Since acetic acid was the only organic chemical present, the total organic carbon (TOC) assay was used to monitor the concentration of acetic acid in the feed and effluent. Typical loadings in wet oxidation VPEs are 100-1000 ppm and it becomes increasingly difficult to achieve lower levels. Initially, as a benchmark, levels of 20-50 ppm were sought, starting with 1000 ppm acetic acid solution.

Experimental conditions are listed below:

Feed Concentration:	1.0 g/L aqueous acetic acid (pH 3.1)
Catalyst:	Pt O_2/Alumina
Weight:	390.0 g
Reactor Volume (total):	2 L
Temperature:	260 ± 10°C
Pressure:	480 psi
Feed Flowrate:	17 mL/min later reduced to 2 mL/min

The liquid feed flowrate was initially measured at 17 mL/min and a run was continued at this flowrate for 95 minutes, at which time the flowrate was reduced to 2.5 mL/min. These pump flowrates were measured against ambient pressure and the corresponding condensed vapour collection rates were found to be 14 and 2.0 mL/min respectively, when working against the reactor operating pressure. The experimental run was then continued at the lower flowrate for a period of 3 hours. Samples of the effluent were taken at 15 and 30 minute intervals during the first and second parts respectively.

The samples were subjected to total organic carbon analysis (TOC). Dissolved carbon dioxide was removed by acidification with HNO_3 and sparging with nitrogen gas. Results are given in Table 5.22.

These results indicate a high and consistent destruction of acetic acid at both flowrates. In order to evaluate the reactive capacity of the catalyst it was necessary to exceed its capacity. The simplest solution (i.e. to increase the feed flowrate) was not available to us since our vaporization capacity was insufficient. It was, therefore, necessary to reduce the catalyst bed volume. This was achieved by implacement of the insert described previously. Previous attempts using simple reduction of the amount of the catalyst were unsatisfactory due to the short vertical path length and channeling in the bed. Also early attempts without the wire mesh cap resulted in catalyst blowout into the headspace. Final experimental conditions are listed below:

Feed Concentration:	1.0 g/L aqueous acetic acid
Catalyst:	Pt O_2/Alumina
Weight:	100 g
Reactor Volume:	200 mL
Temperature:	263 ± 15°C
Pressure:	490 psi
Feed Flowrate	7 mL/min

Analysis by TOC of the feedstock and effluents respectively are given in Table.5.23.

These results indicated that the capacity of the catalyst had, indeed, been exceeded and allowed calculation of the hourly specific catalytic activity (HSCA). This parameter is the mass of acetic acid destroyed per unit mass of catalyst per unit time.

The HSCA was calculated from the following formula:

$$\text{HSCA} = \frac{r \times f}{w} \quad h^{-1}$$

where: r is the fraction of acetic acid destroyed
f is the flowrate of acetic acid in g/h
and w is the weight of catalyst employed under the condition of temperature, pressure and reactant concentration used in this study

The specific reactor volume, V_{sp} has also been calculated on a similar basis from:

$$V_{sp} = \frac{r \times f}{V} \quad \text{g/L-h}$$

V = reactor volume

Results are displayed below:

Sample	HSCA ($h^{-1} \times 10^{-3}$)	V_{sp} (g/L-h $\times 10^{-3}$)
1	1.32	0.66
2	1.12	0.56
3	0.93	0.47
Mean	1.12	0.56

(ii) Other Catalysts

Reference to the literature indicated that several proprietary catalysts had been developed and patented by the Phillips Petroleum Company for the destruction of refractory organics in dilute aqueous streams(10-14).

A request was made to the Phillips Petroleum Company by telephone and in writing in an attempt to obtain a sample of their catalyst for a laboratory trial (see Appendix F). Unfortunately, this request was not fulfilled.

Further work was, therefore, carried out at Ontario Research with catalysts readily to hand. These included samples of pelletized cupric oxide on alumina and pelletized iron oxide on alumina. These are reported separately below:

Copper Oxide - Harshaw

Reactor conditions are listed below:

Feed Concentration:	1 g/L acetic acid
Catalyst:	Pelletized copper oxide on alumina
Weight:	207 g
Reactor Volume:	200 mL
Temperature:	270 ± 13°C
Pressure:	400 psi
Feed Flowrate:	7/20 mL/min

Results of the experiment are given in Table 5.24.

The very high conversion observed in Sample 1 was probably due to preheating of the catalyst bed at the start of the run. Samples 2, 3 and 4 show a representative run at the typical operating temperature and pressure. Increase of the feed flowrate produces a corresponding decrease in the amount of destruction. The HSCA and V_{sp} were calculated and are given in Table 5.25.

The HSCA results obtained compare favourably with those obtained from platinum oxide. The similarity in figures between the HSCA and the V_{sp} are due to the similarity between the catalyst weight and its volume, approximately 1 g/cc in the packed bed. This means that, on a volumetric basis, the copper oxide catalyst is approximately 2 X more effective than the platinum.

The reduction in activity at the higher flowrate reflects the difficulty in maintaining heat supply in our laboratory set-up.

Iron Oxide - Harshaw

Reactor conditions are listed below:

Feed Concentration:	1 g/L acetic acid
Catalyst:	Pelletized iron oxide on alumina
Weight:	A - 208, B - 224 g
Reactor Volume:	200 mL
Temperature:	A - 260 ± 17°C, B - 265 ± 14°C
Pressure:	A - 420, B - 430 psi
Feed Flowrate:	20 mL/min

Results of the experimental runs are presented in Table 5.26.

The decrease in catalyst activity observed in both runs with this catalyst indicated that some process of inhibition was occurring. This could be contributed to chemical reduction of the catalyst, although careful calculation indicated an approximate 20 X excess of oxygen present as supplied by the air flow. A pure oxygen gas supply was attached without improvement in catalyst activity.

Produced Water Vapour Phase Condensate

Up to this point, experiments had been carried out on the aqueous acetic acid model solutions. A sample of vapour phase condensate (VPC) was collected from Wetox treatment of the produced water with the intent of subjecting it to vapour phase catalytic reaction conditions. Unfortunately, the condensate was found to contain significant amounts of hydrocarbon oils which separated on condensation. The vapour phase effluent was found to have a residual COD of 9,000 ppm and this was thought to be too high for further reaction in the catalytic reactor. Also, the VPE as received was not considered typical of what could be expected from an actual operating plant, because wet oxidation temperatures and pressures were lower than that considered optimum. Therefore, experimentation with the vapour phase reaction was concluded at this point.

5.6.3 Vapour Phase Catalysis Study Summary

In summary:

- A laboratory scale reactor system has been designed, constructed, tested and found to operate satisfactorily to destroy refractory organics in water vapour.

- Three catalysts were tested, two of which were found to be acceptable (platinum-alumina and copper oxide-alumina).

- Catalytic activities were found to be similar.

- No attempts were made to optimize the system because of the lack of availability of specialized catalysts. Information from the literature could, however, be used to formulate these in the laboratory.

5.7 Corrosion Tests

This corrosion test program was initiated to evaluate potential materials of construction for a Wetox system treating produced water and solid fuel mixtures. Only quite exotic alloys were selected for testing, the ultimate objective of this relatively short test being to establish acceptable materials for a pilot scale system. Less costly materials would be examined over longer periods of time in the pilot unit for their suitability for commercial scale plants.

5.7.1 Solution Description

Due to various problems (ironically brought about by corrosion), three test series were attempted, with only one being successful. The conditions for all tests were as follows:

- Temperature: approximately 280°C
- Pressure: approximately 14 MPa
- Agitation: 600 rpm
- Solution: 2% fluid coke
  3% sulfuric acid added
  0.4% sodium chloride
  1 L HTS produced water

The 2% coke concentration is the practical maximum that can be employed in Ontario Research's high pressure equipment. This figure is significantly below that anticipated in actual pilot or full scale operation, and, therefore, sulfuric acid was added to simulate higher acidity resulting from higher initial coke concentration. There is also significant evaporation occurring during actual continuous flow testing, causing an effective concentration of produced acids.

The latter argument is also the reason for sodium chloride being added. Evaporation does not occur on a batch scale to the same extent as in a continuous flow process. Thus, concentration effects can only be simulated.

5.7.2 Description of Corrosion Test Coupons

Standard "J" strip corrosion coupons were utilized. These allow for the evaluation of the resistance of the materials to four different types of corrosion as follows(15):

1. General corrosion: samples were weighed before and after and weight loss calculated.

2. Localized Galvanic: Coupons were cut and re-welded for visual evaluation of this corrosion type.

3. Stress Corrosion Cracking: Coupons were bent 180° per ASTM recommended standards.

4. Crevice or Concentration Cell: Coupons were insulated from restraining jig with teflon gaskets. Pitting noted in this area likely due to this corrosion type.

Samples were cleaned before and after immersion in test solution as follows:

1. Ultrasonic bath in Decon 75 concentrate (15-20 minutes)
2. Water and acetone rinse
3. Ultrasonic bath in toluene (15-20 minutes)
4. Acetone rinse

5.7.3 Corrosion Test Program

The first corrosion testing attempt was conducted in a 2 L, Hastelloy C-276 high pressure autoclave. Four coupons were immersed in the solution:

- Carpenter 20 alloy
- Hastelloy C-276
- Titanium Grade 2 (commercially pure)
- Titanium Grade 7 (Ti-Pd alloy)

Within approximately 25 hours after system stabilization, severe leaks were detected around various fittings on the reactor. The unit was subsequently shut down, dismantled and examined. Severe corrosion was apparent on stainless steel plugs as well as the Hastelloy rupture disc (all located in the vapour space of the vessel). Furthermore, both the Carpenter 20 alloy and the Hastelloy C-276 coupons showed considerable pitting and general corrosion. These were weighed, and found to have a weight loss of 1.53 and 0.8 grams respectively. It was obvious, at this point, that corrosion tests could not be undertaken in this unit.

The second attempt at corrosing testing was carried out in a 4.5 L high pressure unit, lined with titanium Grade 2. The head of this vessel is constructed of titanium Grade 5. Only the two titanium coupons, Grades 2 and 7, were immersed in the solution for this test. Again, after about 27 hours of operation, leaks developed around the head gasket. Upon shutdown and disassembly, severe corrosion was observed around bored holes in the reactor head. No corrosion was detected on the titanium Grade 2 liner, and other parts, or, indeed on the two coupons themselves. Two possible reasons for this corrosion phenomenon are:

1. Improper cooling of the head during drilling, which resulted in embrittlement of the titanium Grade 5.

2. Acidic solutions are potentially corrosive to titanium if passifying agents (e.g. heavy metals such as iron, copper, etc.) are not present(16). Thus, the acidic vapours may have condensed on the cooler reactor head, and, since this solution has been effectively distilled, no passifying agents can be present.

The third and final corrosion test series was conducted using a new titanium Grade 12 head, and all parts of the unit were double checked to ensure that they were constructed of titanium Grades 2, 7 or 12. On the advice of Titanium Co. Ltd. (Montreal)(17), Grade 12 coupons were also constructed. This grade has similar corrosion resistant properties to Grade 2, but has higher allowable working stresses at elevated temperature. For this test, six coupons were installed in the unit: three in solution as previously, and three were mounted above the liquid phase, thus allowing the corrosivity of the vapour phase to be evaluated.

This test ran for 482 hours, with one planned shutdown to examine the system. Weight losses determined on the six coupons and the respective corrosion rates are tabulated in Table 5.27. The general corrosion rates were calculated as follows:

$$\text{Corrosion Rate (mm/year)} = \frac{K \times W}{A \times T \times D}$$

where K = 876×10^4
W = weight loss or gain (g)
T = exposure time (hours)
A = coupon surface area (cm^2)
D = coupon density (g/cm^3)

A corrosion rate of less than 0.1 mm/year is considered acceptable(18). In this test program, the three grades of titanium were substantially below this maximum. In addition, no visual signs of galvanic, stress corrosion or pitting were observed on any of the coupons.

5.7.4 Discussion

The major objective of this short corrosion test program was to establish potential construction materials which could be used in a pilot plant designed to treat solid fuel/produced water slurries. This unit would have the capability to accept corrosion coupons mounted in different locations within the vessel to evaluate corrosion over longer time periods.

Either relatively high sulfuric acid or chloride concentrations, in themselves, are potentially corrosive to many alloys. However, few alloys are able to resist the corrosivity of the two together. Titanium Grade 12 would probably be the preferred construction material, based on cost, for a full scale system. For a pilot plant, it is believed that the more exotic Grade 7 should be employed. Subsequent longer term corrosion testing would confirm the suitability of other materials (e.g. Titanium Grade 12).

TABLE 5.1 - Produced Water Sample Analyses

Sample I.D.	COD (%)	SCOD (mg/L)	SS (%)	TS (%)	VSS (% of SS)	VS (% of TS)	TOS (%)	Cl^- (mg/L)	SO_4 (mg/L)	Ash (%)	Oil & Grease (g/L)	
											Total	Soluble
PW-1	30-40	3,125	7.5	8.41	~ 100	98.2	0.91	500	185	1.8	6.1	.370
Aqueous				0.5							0.15	
PW-2	17.6	5,750	3.5	3.83	~ 100	96.3	0.33	430	165	3.7	~ 3.83	.260
Aqueous				0.36							0.13	
HTS	0.7-1.2										~ 0.15	
CLPW	0.2-1.1			1.4							~ 0.1	
P-34	0.3-0.6										~ 0.1	

TABLE 5.2 - PW-1 Kinetics: No Additions

Injection	Temperature (°C)	K_1 (min^{-1})	r_1	K_2 (min^{-1})	r_2	Rate Change Time (mins)
Yes	240	0.028	0.989	0.009	1.0	20.0
No		0.0176	0.98	0.0055	∿ 1	21.5
Yes	260	0.084	0.99	0.021	0.99	9.5
No		0.042	0.97	0.003	0.989	13.2
Yes	280	0.105	0.98	0.011	1.0	9.0
No		0.056	0.998	0.0014	0.963	11.0
Yes	290	0.115	0.955	0.006	1.0	12.5

TABLE 5.3 - Arrhenius Parameters

	Below 260°C			Above 260°C		
	E (cal/mole)	A (min^{-1})	r	E	A	r
Injected Runs	29,889	1.45×10^{11}	1.0	6298	31.9	$\sim$1
Non-Injected Runs	23,663	2.05×10^{8}	1.0	8437	119.6	1.0

E - Activation Energy (cal/mole)

A - Frequency Faction (min^{-1})

r - Correlation coefficient

TABLE 5.4 - Kinetics of PW-1: Copper Catalyst & pH Adjusted Runs

Temperature (°C)	Injection	Additions	K_1 (min-1)	K_2 (min-1)	Rate Change Time (mins)	COD Reduction (%)	
						Rate Change	30 mins
220	No	Copper	0.038	0.012	13	46.0	54.0
	No	H_2SO_4	0.035	0.012	19		
240	No	Copper	0.056	($r < 0.95$)	15	68.8	73.8
	Yes	Copper	0.065	0.009	12	44.9	54.1
	No	H_2SO_4	0.047	0.008	17		
	Yes	H_2SO_4	0.05	0.019	20		
260	No	Copper	0.092	($r < 0.95$)	15	74.3	77.8
	No	H_2SO_4	0.066	0.008	12	56.7	61.7
	No	None	0.042	0.003	13		

TABLE 5.5 - Arrhenius Parameters

	PW-1 Effect of Additives*		
	E (cal/mole)	A (min^{-1})	r
No additions	-23,663	2.05×10^8	1.0
Copper Catalyst (250 mg/L)	-11,560	4988	0.986
pH + 2	- 8,290	163	0.993

*Below 260°C

TABLE 5.6 - Arrhenius Parameters - "Other" Produced Water Samples

Produced Water Code	Activation Energy (cal/mole)	Frequency Factor (min^{-1})	r
HTS	5248	6.7	0.969
P-34	15120	31126	0.99
CLPW	24538	4.42×10^8	~1

TABLE 5.7 - Single Compartment Continuous Flow Test

	Feed Flowrate (mg/min)	COD		Oil & Grease		% Destruction	
		(mg/L)	(mg/min)	(mg/L)	(mg/min)	COD	Oil & Grease
Feed	385	7170	2760	2388	919	-	-
LPE	335	4275	1432	556	186	-	-
VPE	50	3290	165	660	33	-	-
LPE + VPE	385	-	1597	-	219	42.1	76.2

TABLE 5.8 - 4-Compartment Reactor Test Conditions

Waste Feed:	Athabasca HTS + ∿ 1.0 g/L $CuSO_4$		
Waste Pumping Rate:	Water Flow Rate - .483 L/min COD Flow Rate - 3.93 g/min COD		
Reactor Residence Time:	78 minutes		
Reactor Pressure:	650 psi - 4.48 MPa		
		scfm	
Air Flow Rate:	Compartment #1	.46	13.0 L/min
	2	.07	1.98
	3	.03	.85
	4	.03	.85
Temperature Profile:	Compartment #1	480	249°C
	2	468	242
	3	445	230
	4	445	230
Water Balance:	Measured Liquid Produced - .460 L/min. Measured Steam Produced - .023 L/min.		
Oxygen Balance:	Measured O_2 Concentration in Exhaust - 12% Oxygen Consumed as Fraction of Supplied - 42.9% Total Oxygen Consumed - 2.0 g/min.		

TABLE 5.9 - Produced Water - Pilot Plant Test Results

	Water Balance		COD Balance					Oxygen Balance	
	Liquid ml/min	Steam ml/min	Measured COD mg/L	Calculated Total COD mg/L	Total COD Remaining mg/min	Total COD Removed mg/min	Percent of Feed COD Removed	Oxygen Supplied mg/min	Oxygen Consumed mg/min
Feed	483		8145	8145	3934				
Compartment #1	427.2	55.8	2255	2955	1427	2490	63.4	3630	-
Compartment #2	447.8	35.2	2130	2580	1246	190	4.8	550	-
Compartment #3	464.9	18.1	715	999	483	760	19.3	240	-
Compartment #4	463.9	19.1	1005	1293	625	-130	-3.3	240	-
LPE	460.0	-	750	1109	1	89	2.3		
VPC		23.0	8300		536				
Totals						3399		4660	2000

1. Calculated COD = $\frac{\text{LPE}}{\text{Feed}}$ x LPE COD x $\frac{\text{VPE}}{\text{Feed}}$ x VPE COD

2. COD Remaining = Calculated COD x Feed Rate (L/min)

TABLE 5.10 - 4-Compartment Reactor Test Conditions

Waste Feed:	Athabasca Hts (No Catalyst Addition)		
Waste Pumping Rate:	Water Flow Rate - .590 L/min		
	COD Flow Rate - 4.8 g/min COD		
Reactor Residence Time:	61.0 min		
Reactor Pressure:	650 psi - 4.48 MPa		
		scfm	
Air Flow Rate:	Compartment #1 -	.46	- 13.0 L/min
	2 -	.07	- 1.98
	3 -	.03	- .85
	4 -	.03	- .85
Temperature Profile	Compartment #1 -	480	- 259°C
	2 -	476	- 246
	3 -	456	- 235
	4 -	460	- 238
Water Balance:	Measured Liquid Produced - .54 L/min.		
	Measured Steam Produced - 0.50 L/min.		
Oxygen Balance	Measured O_2 Concentration in Exhaust - 10.0%		
	Oxygen Consumed as Fraction of Supplied - 52.4%		
	Total Oxygen Consumed - 2.4 g/min.		

TABLE 5.11 - Delayed Coke Sample Analyses*

Moisture		Nil
Fixed Carbon		81.74%
Volatile Matter		13.9%
Ash		4.36%
Heating Value	(gross)	30.38 MJ/kg
	(sulfur corrected)	30.09 MJ/kg
Carbon		80.74%
Hydrogen		4.31%
Sulfur:	(Leco)	5.6%
	(Bomb)	4.9%
	(Pyrytic)**	0.2%
	(Sulfate)**	0.0%
	(Organic)**	5.59
	(Total-Leco)**	5.79%
Nitrogen		1.46%

* Performed by General Testing Laboratories, Toronto, Ontario
**Performed by Energy, Mines & Resources, Coal Laboratories

TABLE 5.12 - Delayed Coke - Comparison of Sulfur & Carbon Oxidation Kinetics

Temperature (°C)	Sulfur		Carbon	
	k	r	k	r
240	0.015	.973	0.013	0.998
260	0.03	.987	0.028	∼ 1
280	0.067	.996	0.052	.992

k = specific reaction rate constant (min^{-1})

r = correlation coefficient

TABLE 5.13- Delayed Coke Kinetics
No Additions (100 mesh)

Temperature (°C)	K_1 (min^{-1})	K_2 (min^{-1})	Rate Change Time (min)	COD Reduction (%)	
				Rate Change	150 min
220	0.0092	-	-	-	74.0
240	0.013	-	-	-	86.6
260	0.028	*	92	90.3	91
280	0.052	0.001	∿ 62	∿ 98	∿ 99
290	0.058	0.003	60	97.3	97.9
300	0.045	**	**	**	98.1
320	0.1096	**	**	**	98.2

* Correlation coefficient < 0.95

** Insufficient data points beyond 1st reaction

TABLE 5.14 - Delayed Coke - Arrhenius Parameters
(No Addition)

Mesh Size	Activation Energy (cal/mole)	Frequency Factor (min^{-1})	r
60	26,043	1.17×10^9	.998
100	15,167	44103	.993
250	17,145	3.24×10^5	0.994

* not including questionable 300°C data point

TABLE 5.15 - Kinetics of Fluid Coke

No Addition

Temperature	Injection	K_1	r	k_2	r_2	Initiation Time (min)	Rate Change Time (min)	COD Reduction at Rate Change
240	No	0.013	0.985	-	-	60	-	75 *
	Yes	0.011	0.98			60	-	65.9*
260	Yes	0.02	~ 1	-	-	60	-	89.2*
280	Yes	0.033	~ 1	0.008	1.0	30	108	92.5
300	No	0.06	~ 1			0		93.5*
320	No	0.136	0.997	0.008	1.0	0	19	94.6

* At end of Reaction

k = specific reaction rate constant (min^{-1})

r = correlation coefficient

TABLE 5.16- Fluid Coke - Effect of Particle Size on Arrhenius Parameters

Mesh Size	Activation Energy (cal/mole)	Frequency Factor (min^{-1})	r
60	10,301	327	∿ 1
100	17,927	452,160	0.989
250	24,328	3.41×10^8	∿ 1

TABLE 5.17- Athabasca Pitch Kinetics

No Additions (100 mesh)

Temperature (°C)	K_1 (min^{-1})	r_1	K_2	r_2	Δ Rate Change (min)	COD Reduction
220	0.0078	0.97	-	-	-	53.3
240	0.02	0.993	-	-	-	82.2*
260	0.04	0.98	-	< 0.95	∿ 55	∿ 90 **
280	0.065	0.998	.005	1.0	32	89.5**
320	0.218	1.0	0.018	0.982	7	80.0**

* At end of test

** At rate change

k = specific reaction rate constant (min^{-1})

r = correlation coefficient

TABLE 5.18 - Athabasca Pitch - Arrhenius Parameters

	Activation Energy (cal/mole)	Frequency Factor (min^{-1})	r
No Additions -			
-100 mesh	18,913	2.025×10^6	0.997
-250 mesh	16,429	1.627×10^5	0.973
Copper Catalyst (200 mg/L)	19,609	7.78×10^6	0.994
Sulfuric Acid pH + 2	26,964	5.99×10^9	∿1

TABLE 5.19 - Arrhenius Parameters

Asphaltines

Conditions	Activation Energy (cal/mole)	Frequency Factor (min^{-1})	r
No Additions	6,612	12.7	0.989
With Copper Catalyst	17,585	1.72×10^6	0.99

TABLE 5.20 - Mixed Waste Kinetics - 280°C

Condition	Initial Reaction Rate Constant (min^{-1})	
	Actual	Calculated
HTS + Delayed Coke + Cu	0.058	0.074
HTS + Fluid Coke	0.028	0.04
HTS + Fluid Coke + Cu	0.034	0.06

TABLE 5.21 - Mixed Waste - Arrhenius Parameter

Condition	Activation Energy (cal/mole)		Frequency Factor (min^{-1})	r
	Actual	Calculated		
HTS + Delayed Coke + Cu	7,908	9,297	74.7	0.998
HTS + Fluid Coke	15,834	13,564	48,243	0.982
HTS + Fluid Coke + Cu	9,018	12,722	123	1.0

TABLE 5.22 - PtO_2 Catalyst - Run #1 Results

Sample	Time (min)	Flowrate (mL/min)	TOC (mg/L)	% Destroyed
Feed	-	-	430	0
1	15	17	45	89.5
2	30	17	48.5	88.7
3	45	17	18.5	95.7
4	60	17	15.0	96.5
5	30	2	16.5	96.2
6	60	2	31.5	92.7
7	90	2	30.0	93.0

TABLE 5.23 - PtO_2 Catalyst - Run #2 Results

Sample	Time (min)	Flowrate (mL/min)	TOC (mg/L)	% Destroyed
Feed	-	-	430	0
1	30	7	295	31.4
2	60	7	315	26.7
3	90	7	335	22.1

TABLE 5.24 - Copper Oxide Catalyst Results

Sample	Time (min)	Flowrate (mL/min)	TOC (mg/L)	% Destroyed
Feed	-	-	430	0
1	15	7	24	94.4
2	40	7	165	61.6
3	55	7	200	53.5
4	70	7	197	54.2
5	100	20	390	9.3
6	115	20	325	24.4
7	130	20	265	38.4
8	145	20	305	29.1

TABLE 5.25 - Copper Oxide - HSCA & Usp

Sample	HSCA ($h^{-1} \times 10^{-3}$)	V_{sp} ($g/L\text{-}h \times 10^{-3}$)
1	1.92	1.92
2	1.25	1.25
3	1.09	1.09
4	1.10	1.10
Mean 2, 3, 4	1.15	1.15
5	0.19	0.19
6	0.50	0.50
7	0.78	0.78
8	0.59	0.59
Mean 6, 7, 8	0.62	0.62

TABLE 5.26 - Iron Oxide Catalyst Results

Sample	Time (min)	Flowrate (mL/min)	TOC (mg/L)	% Destroyed
Run A				
1	20	20	13	97.0
2	35	20	47.6	88.9
3	65	20	53.0	87.7
4	80	20	151.0	64.9
Run B				
Feed	-	-	370	0
1	10	20	21	95.1
2	30	20	135	68.6
3	90	20	292	32.1
4	110	20	328	23.7
5	150	20	335	22.1
6	180	20	420	2.3
7	240	20	388	9.8

TABLE 5.27 - Corrosion Test Results

Titanium Grade	Weight Loss (gain) (g)		Corrosion Rate (mm/year)	
	Vapour Phase	Liquid Phase	Vapour Phase	Liquid Phase
2	(0.0012)	0.004	0.00175	0.005
7	(.0007)	0.0011	0.00104	0.00157
12	(0.0018)	0.0033	0.00257	0.00475

FIGURE 5.1

PW-1 KINETICS (INJECTION)

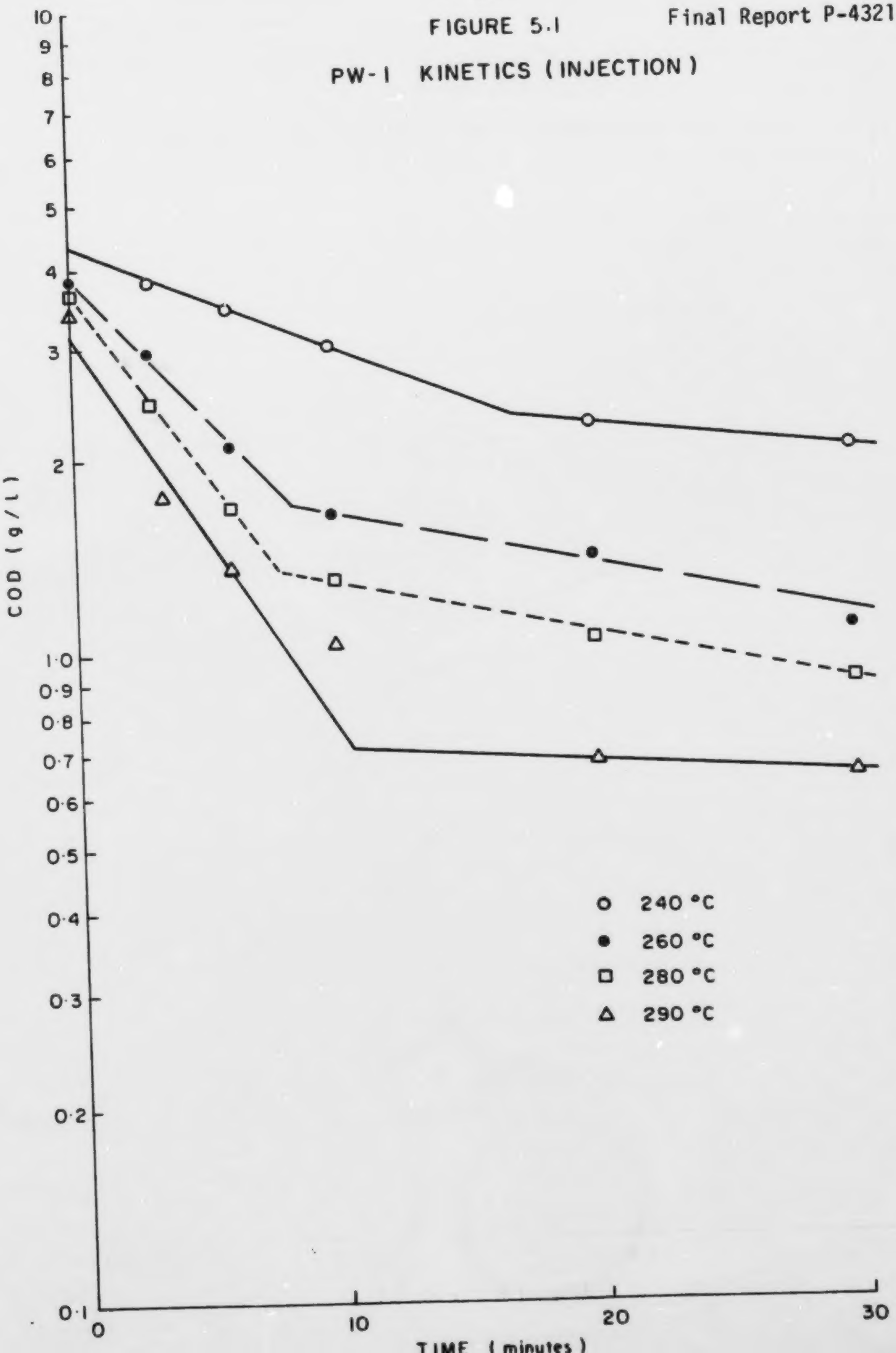
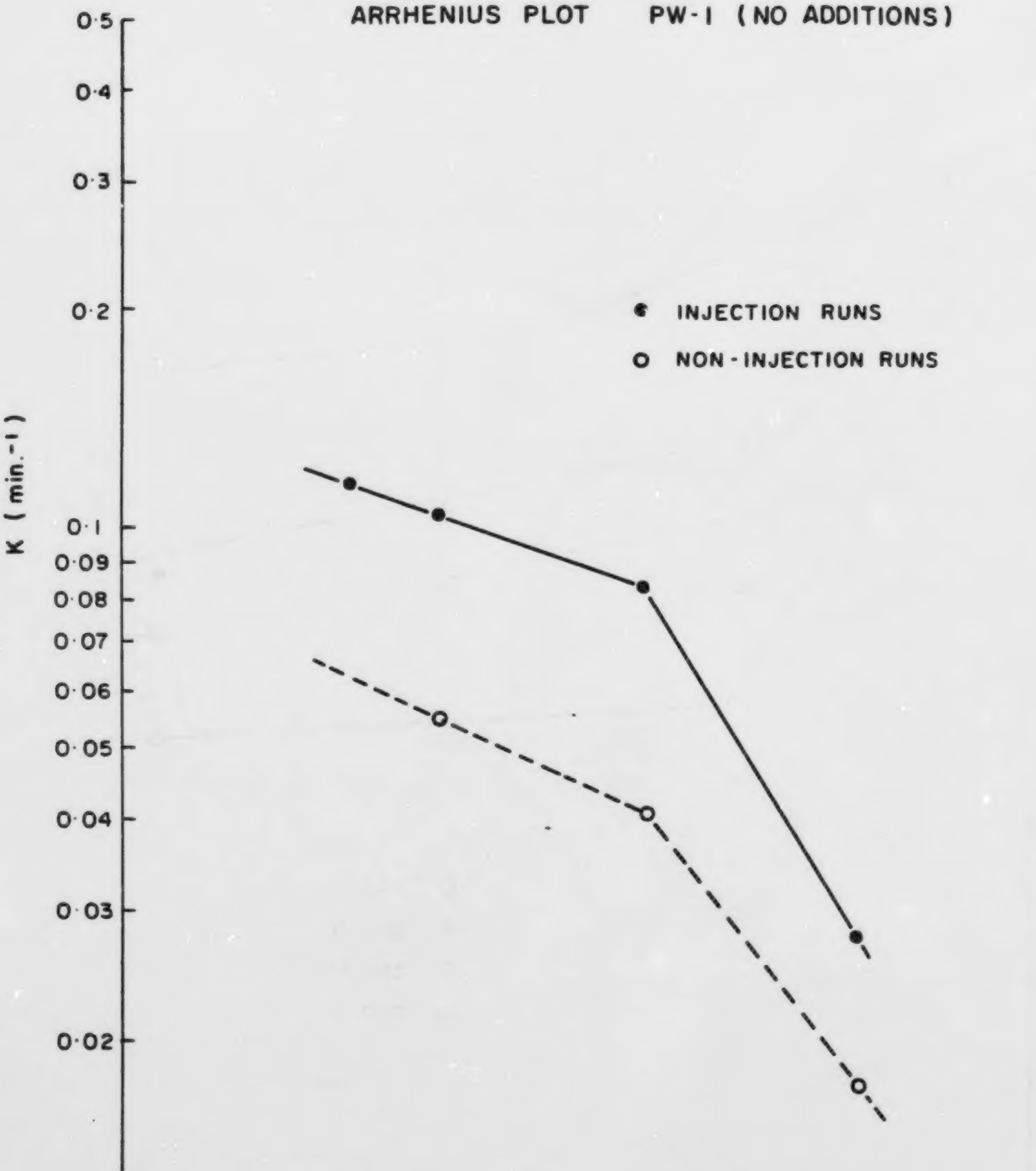


FIGURE 5.2

ARRHENIUS PLOT PW-I (NO ADDITIONS)



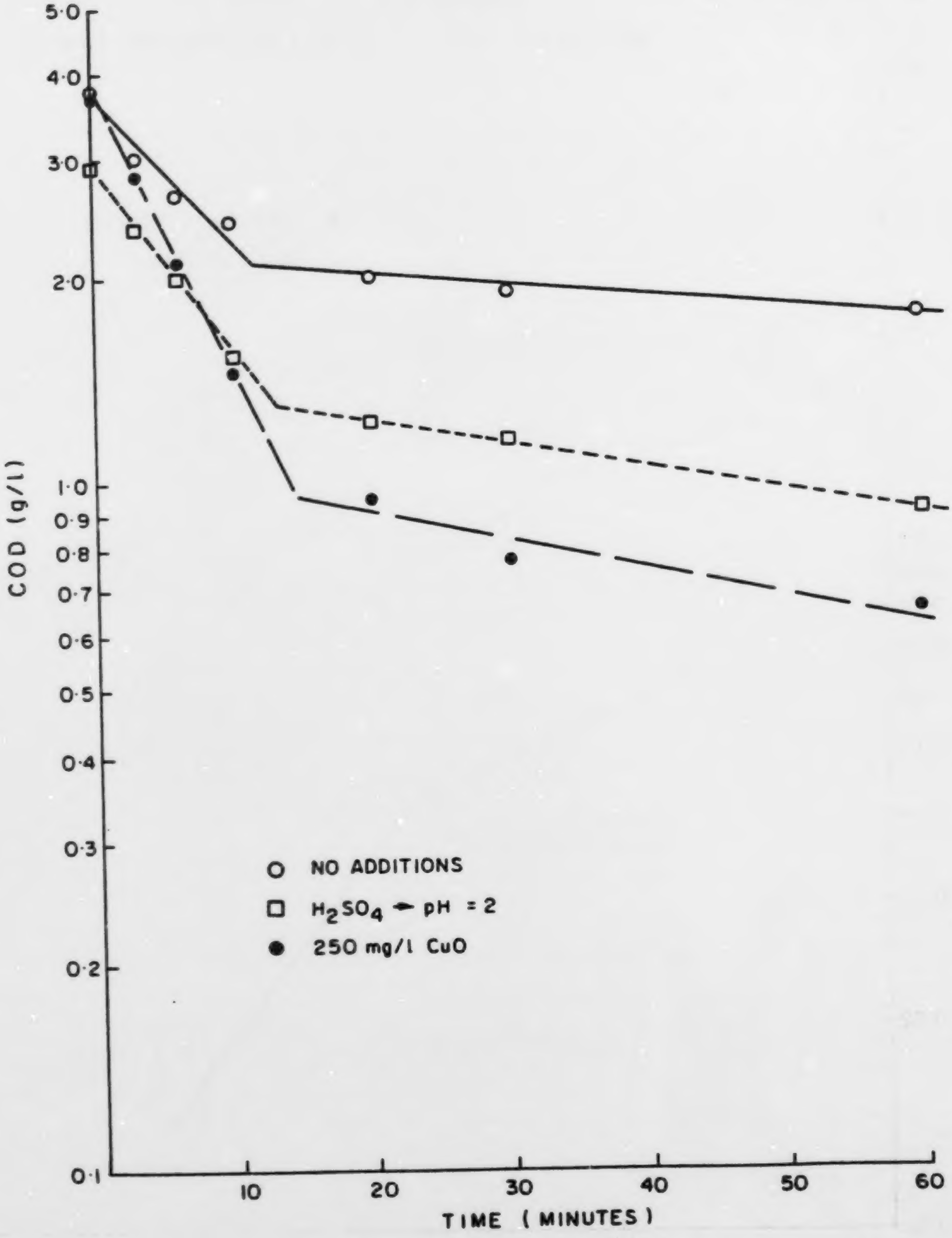


FIGURE 5·3 PW·1 : EFFECT OF ADDITIONS AT 260 °C

FIGURE 5.4

ARRHENIUS PLOT - EFFECT OF ADDITION (PW-1)

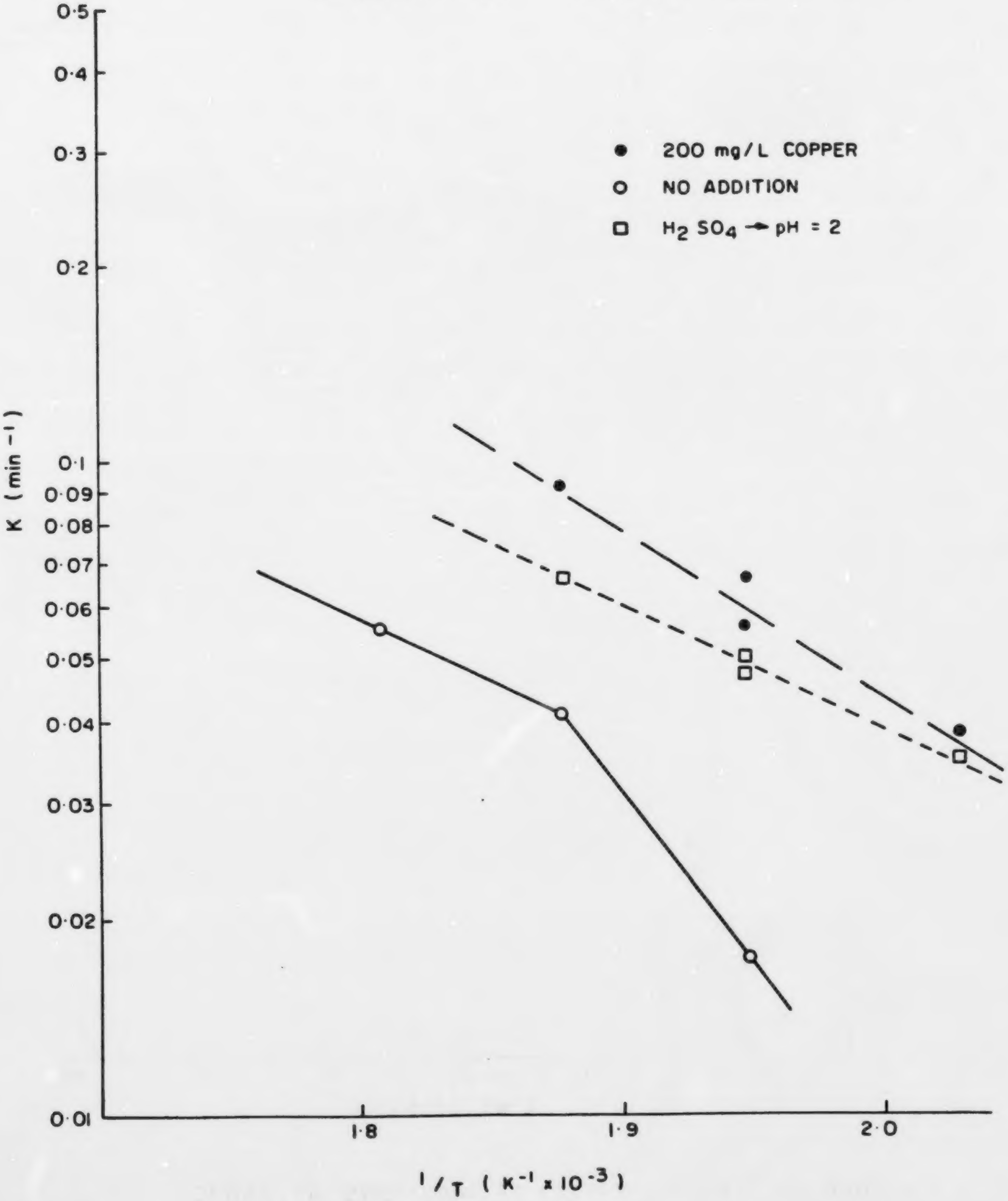


FIGURE 5.5
ARRHENIUS PLOT
" OTHER " PRODUCED WATER SAMPLES

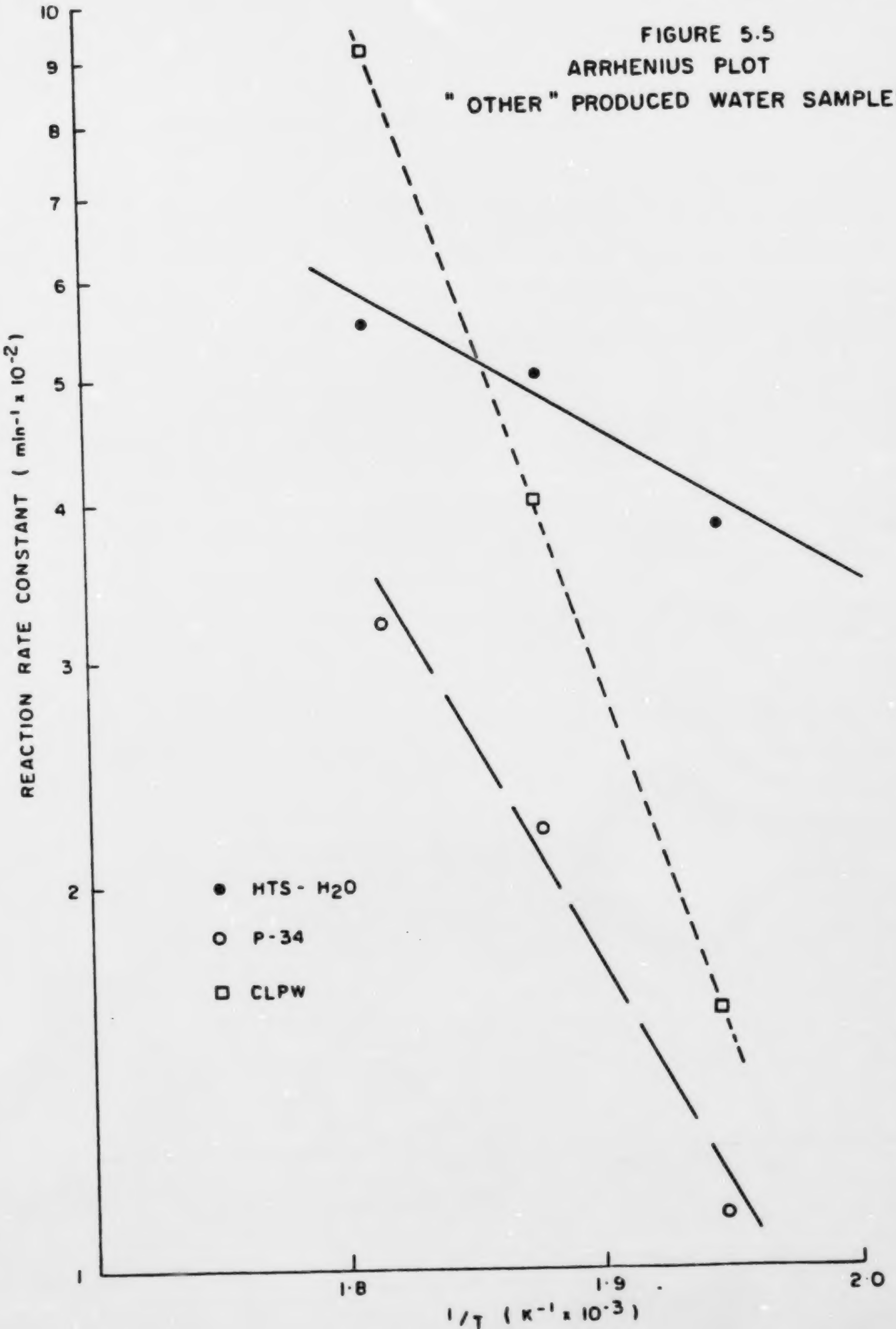


FIGURE 5.6

DELAYED COKE - 240°C

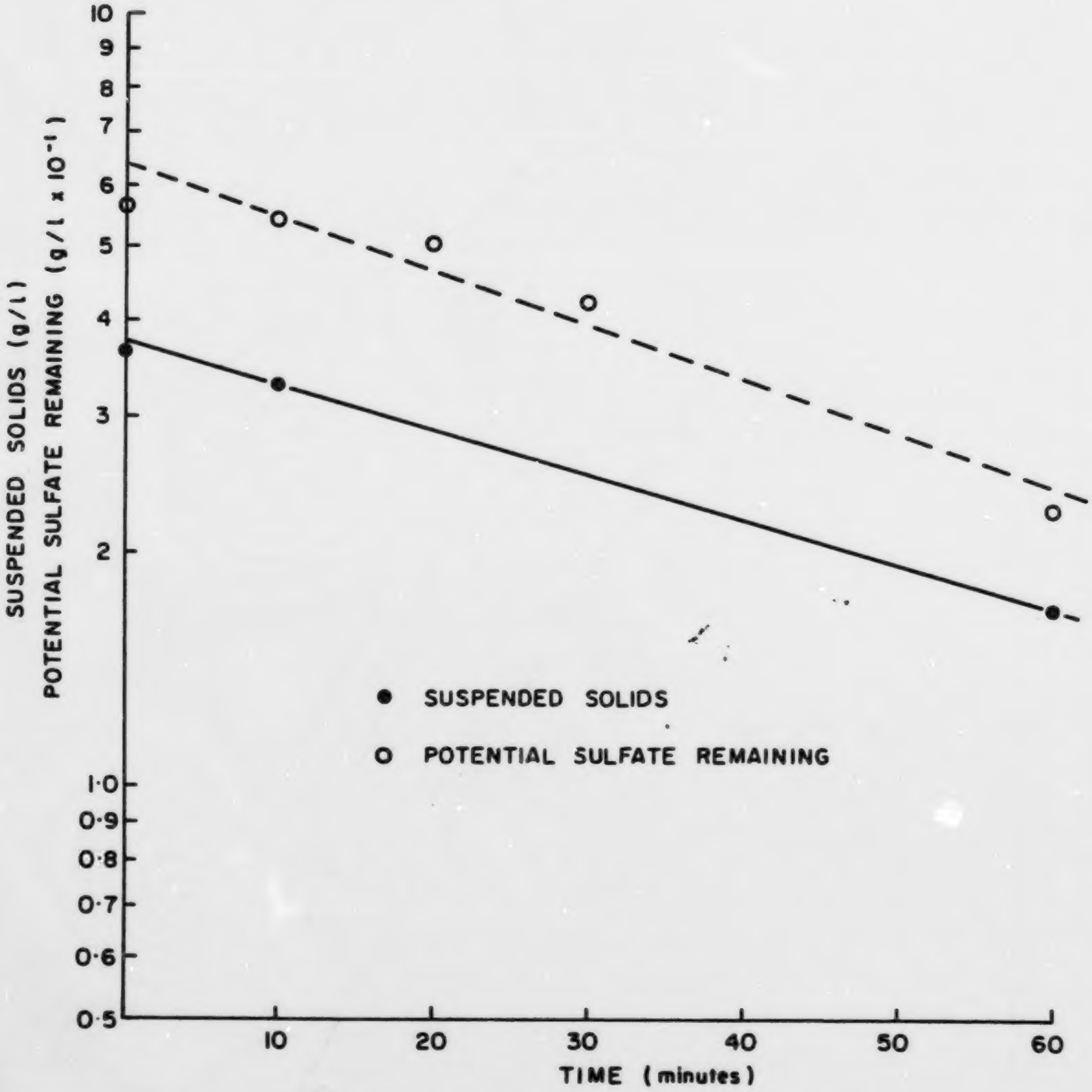


FIGURE 5·7

DELAYED COKE · 260°C

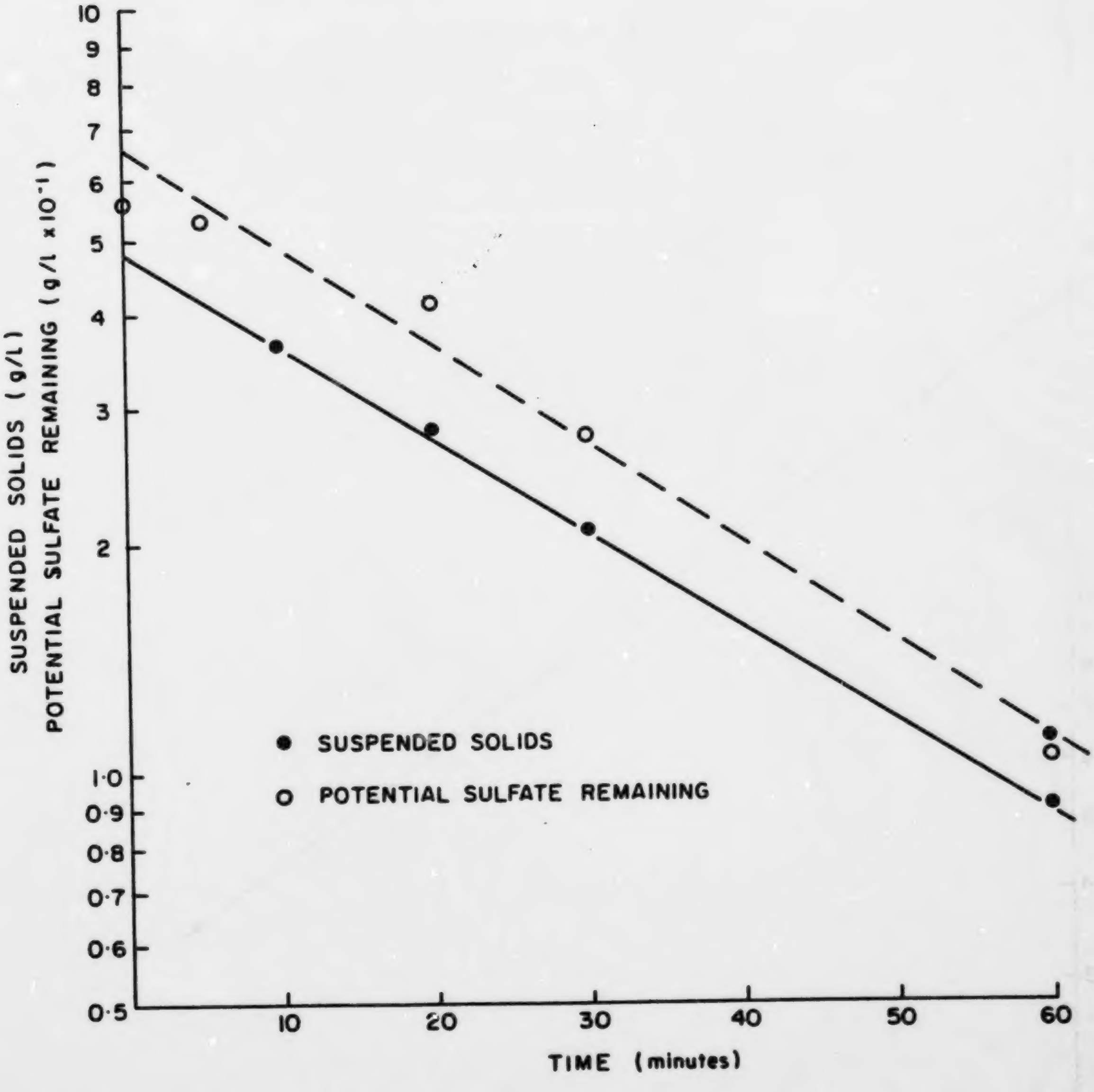


FIGURE 5.8

DELAYED COKE - 280°C

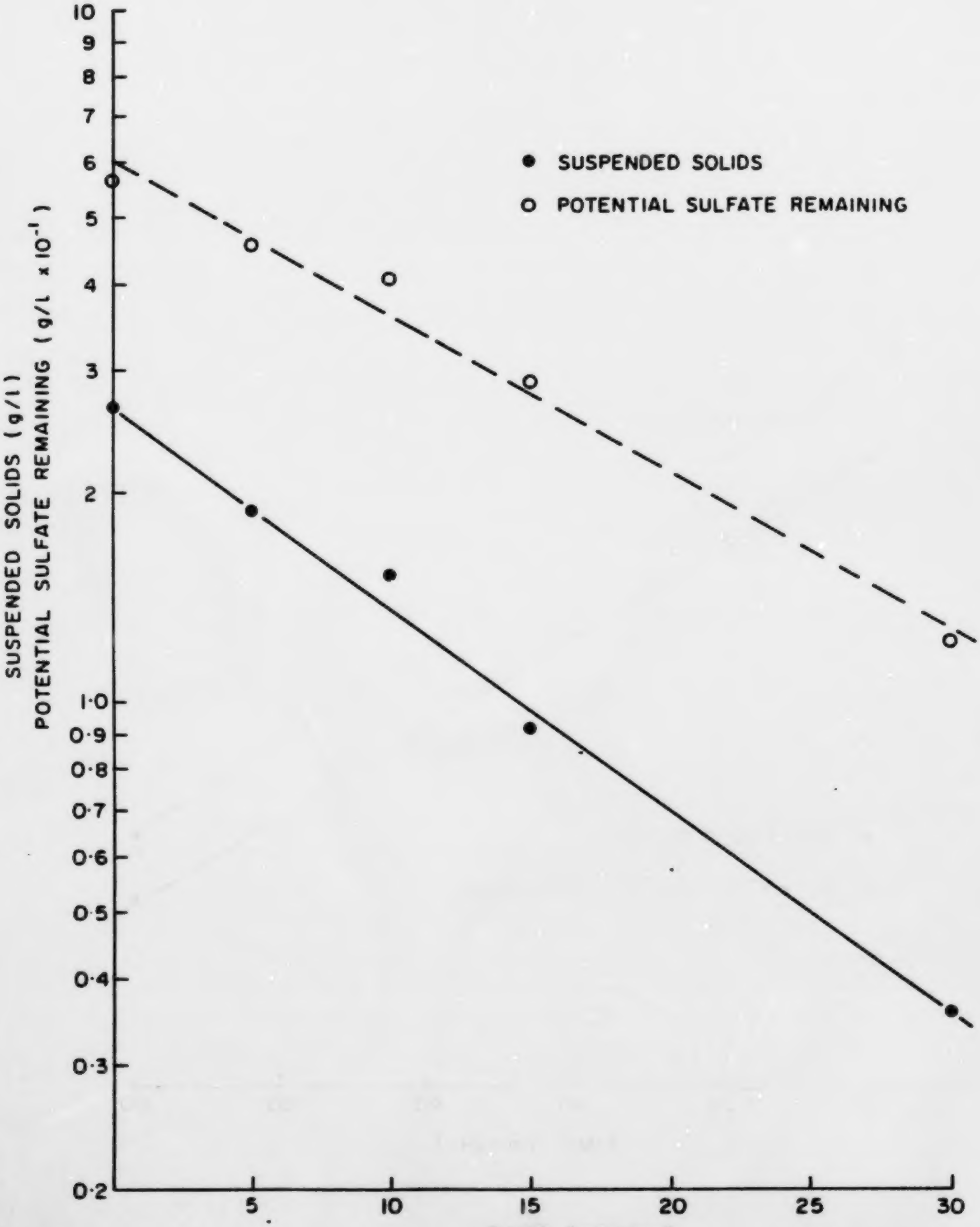


FIGURE 5·9

DELAYED COKE KINETICS
240°C and 290°C

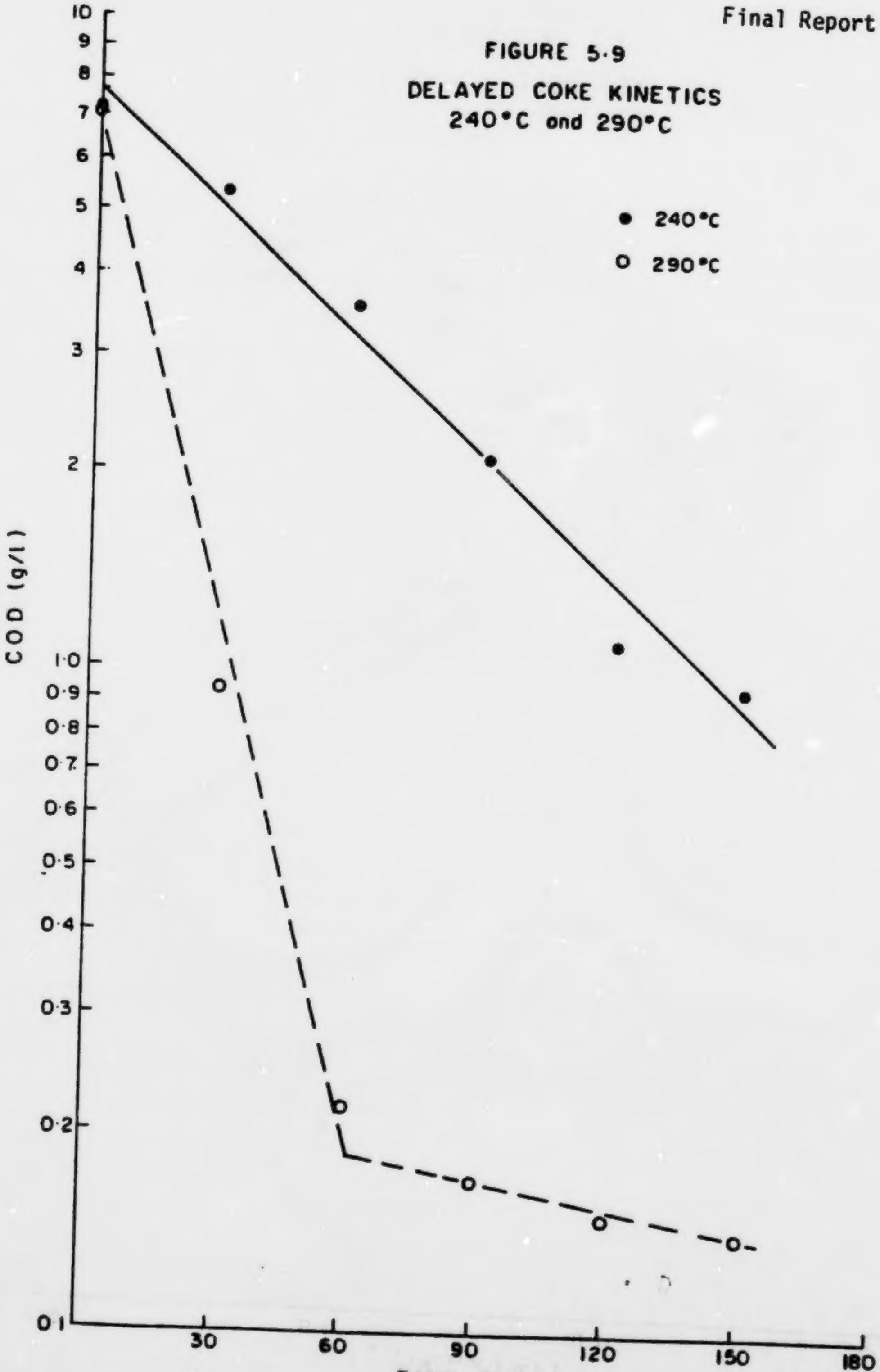
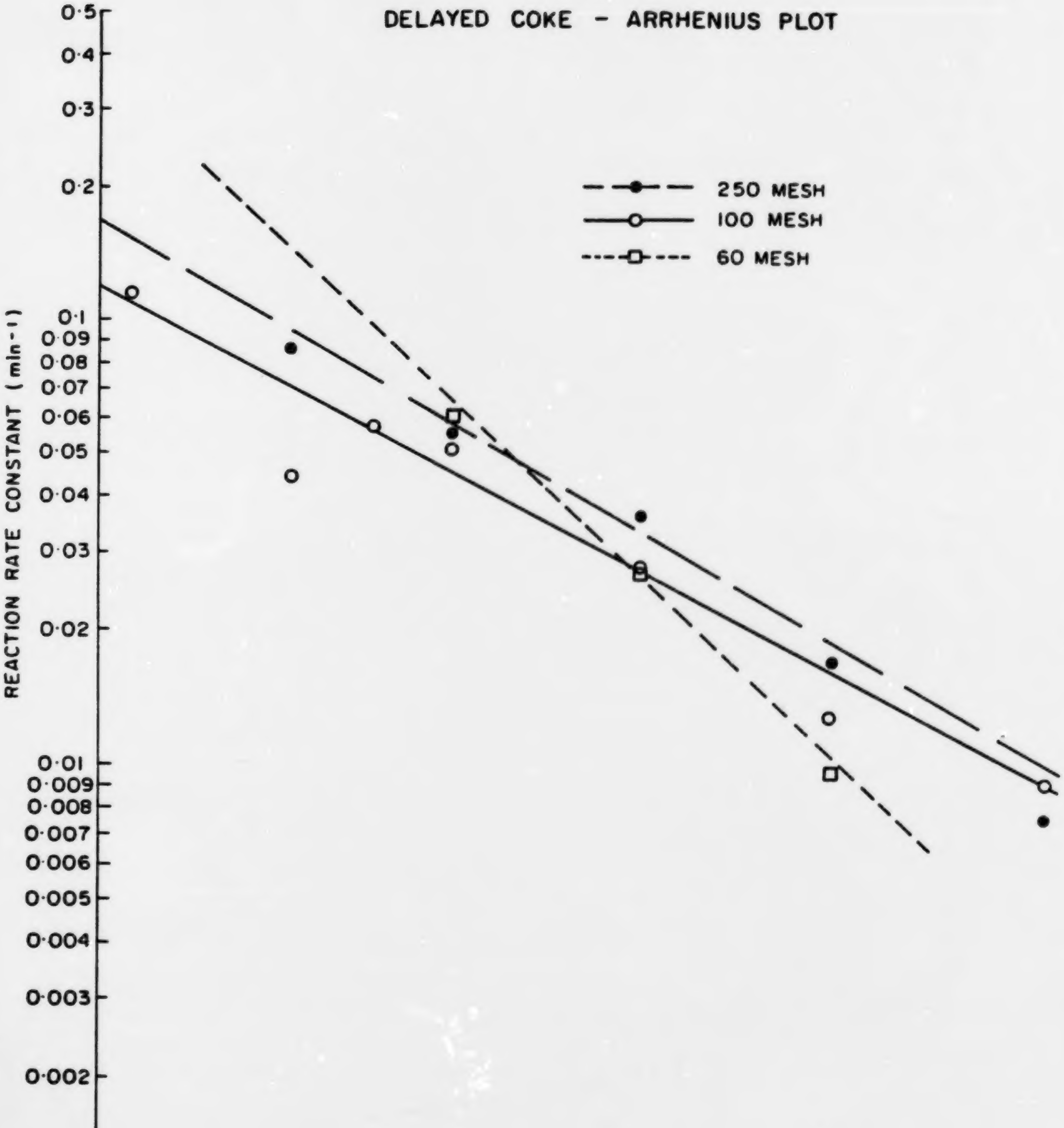


FIGURE 5-10



DELAYED COKE - ARRHENIUS PLOT

FIGURE 5·11

DELAYED COKE
EFFECT OF NaOH ON RATE CONSTANT
AT 260 °C

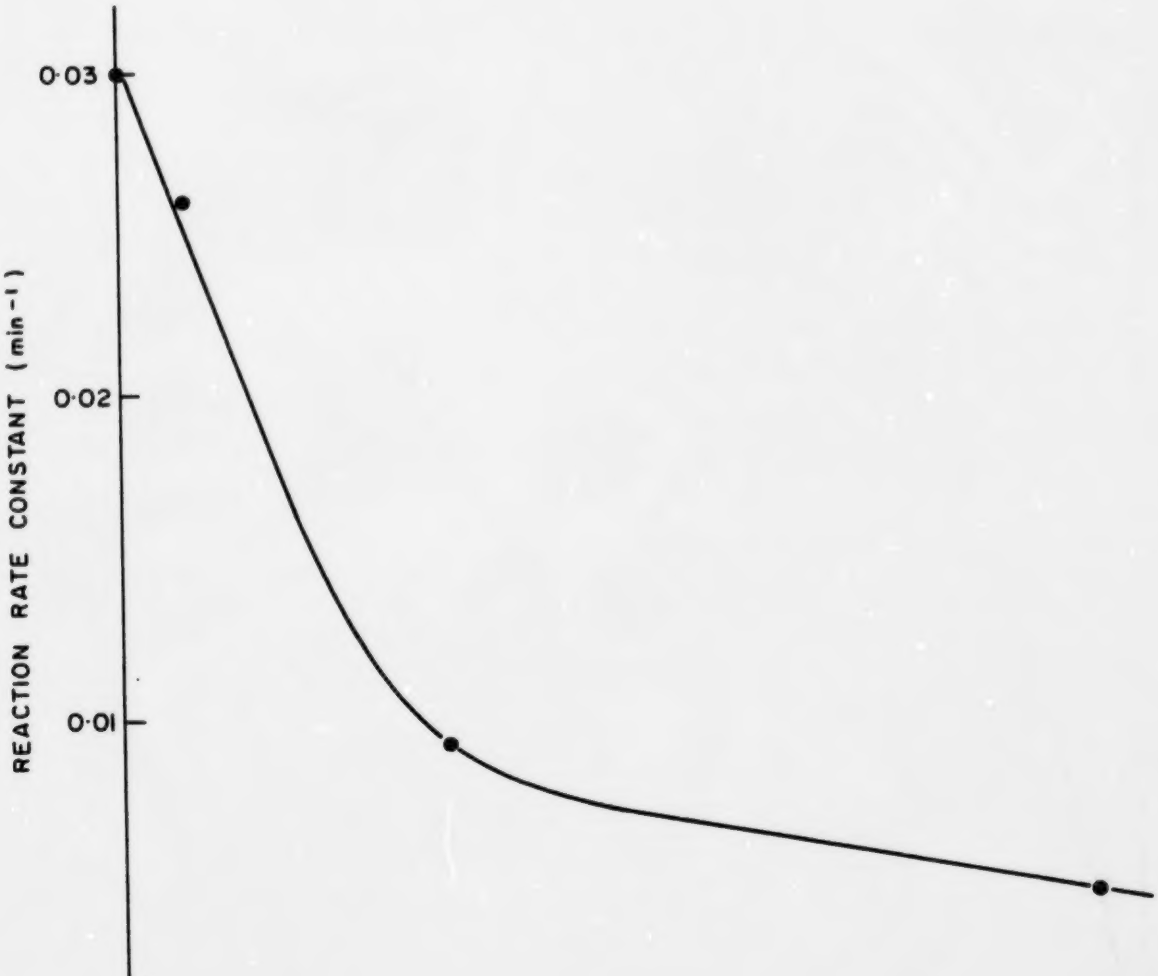


FIGURE 5·12

DELAYED COKE
EFFECT OF O_2 PRESSURE
AT 260°C

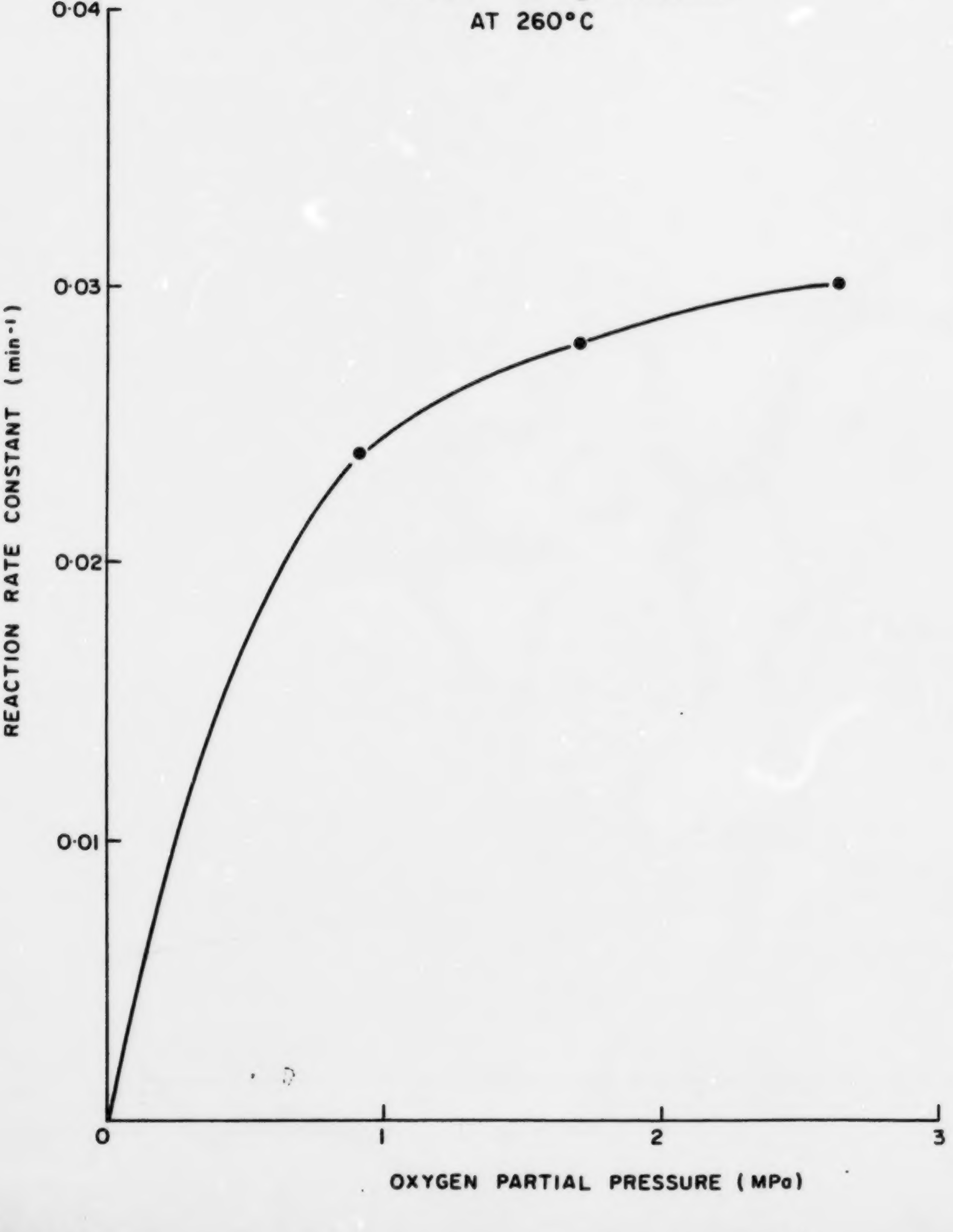


FIGURE 5.13

FLUID COKE KINETICS
240, 260, 280°C

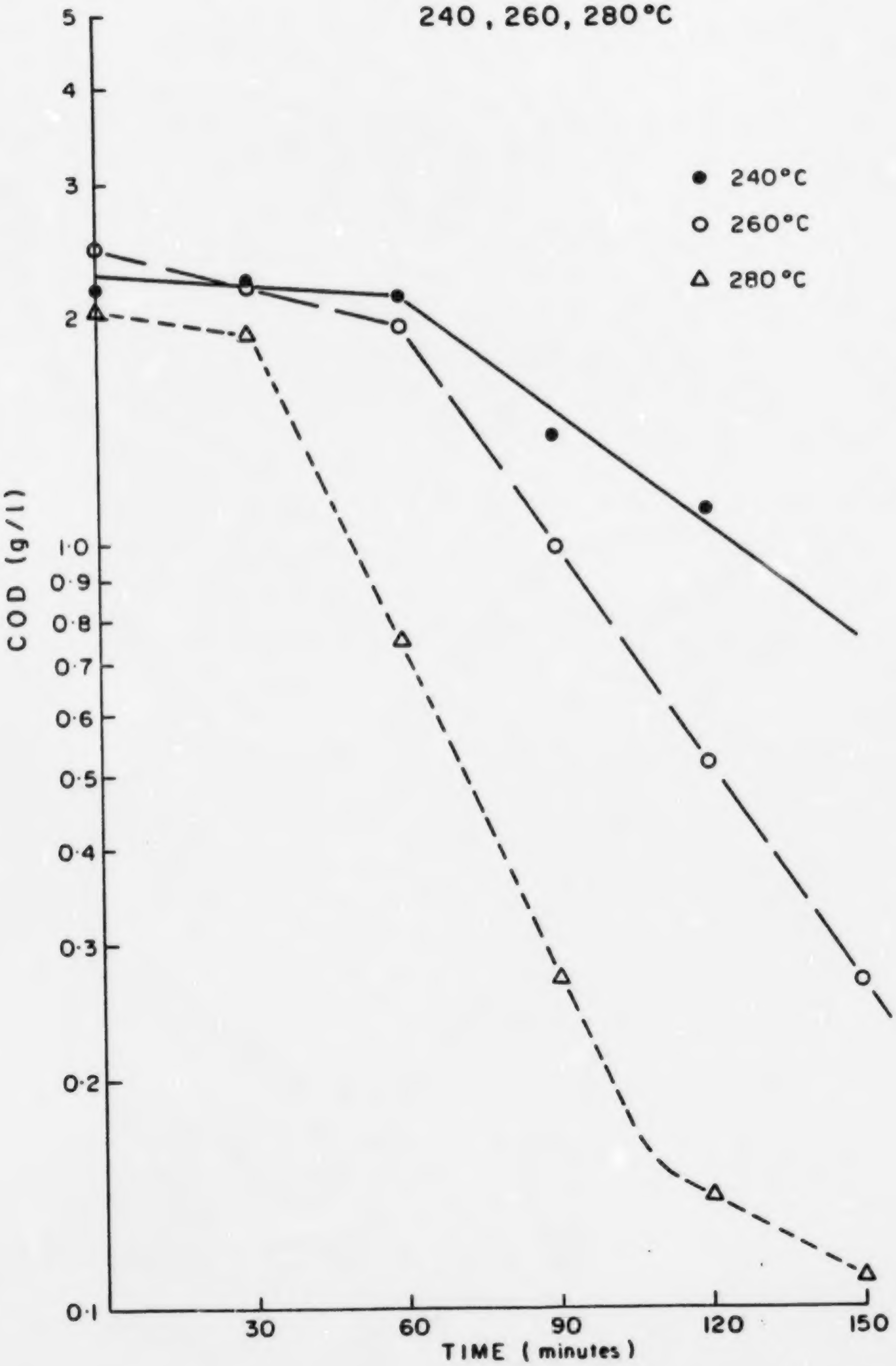


FIGURE 5.14

FLUID COKE KINETICS
300, 320°C

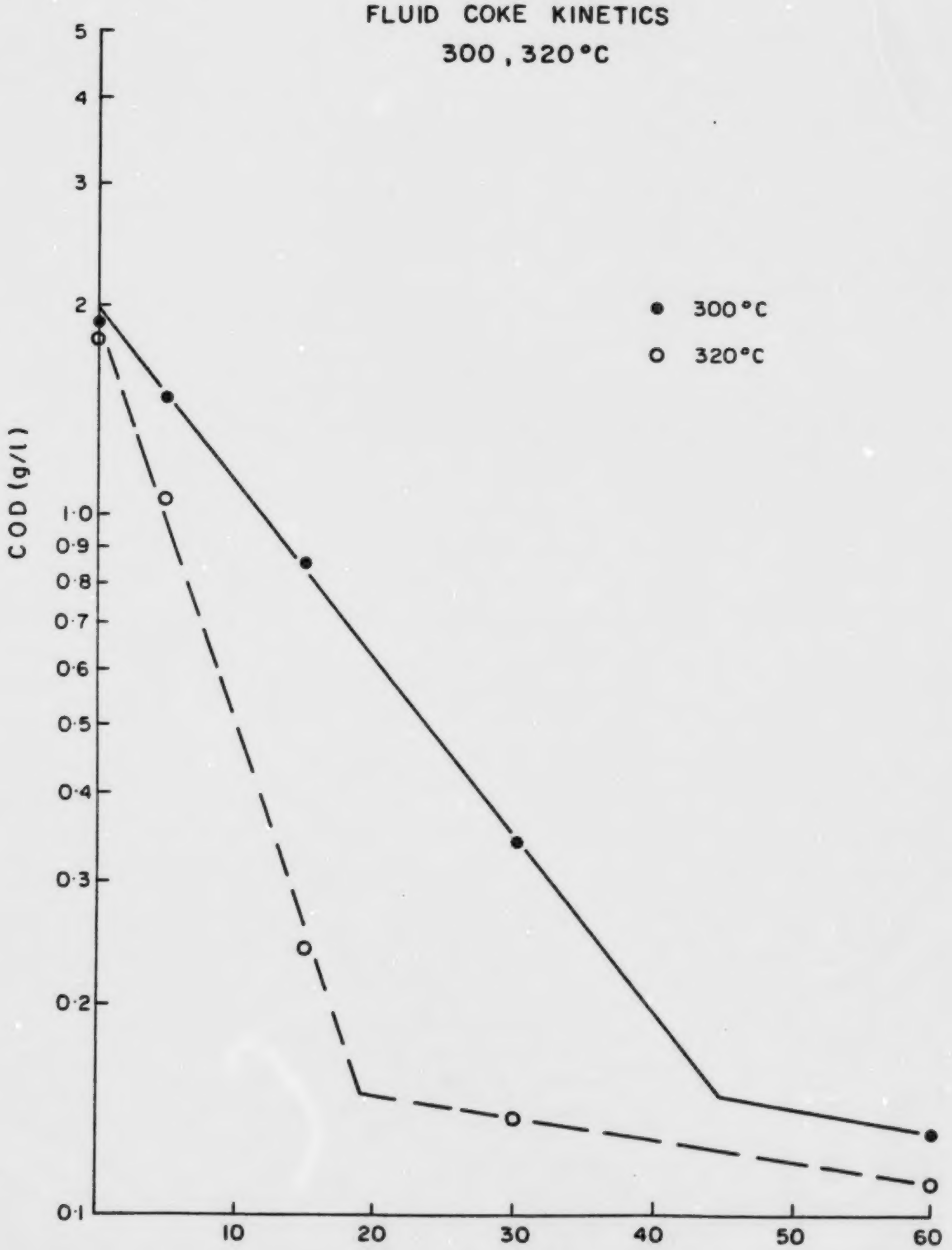


FIGURE 5.15

EFFECT OF PREHEAT AND SURFACTANT ADDITION ON FLUID COKE OXIDATION (260°C)

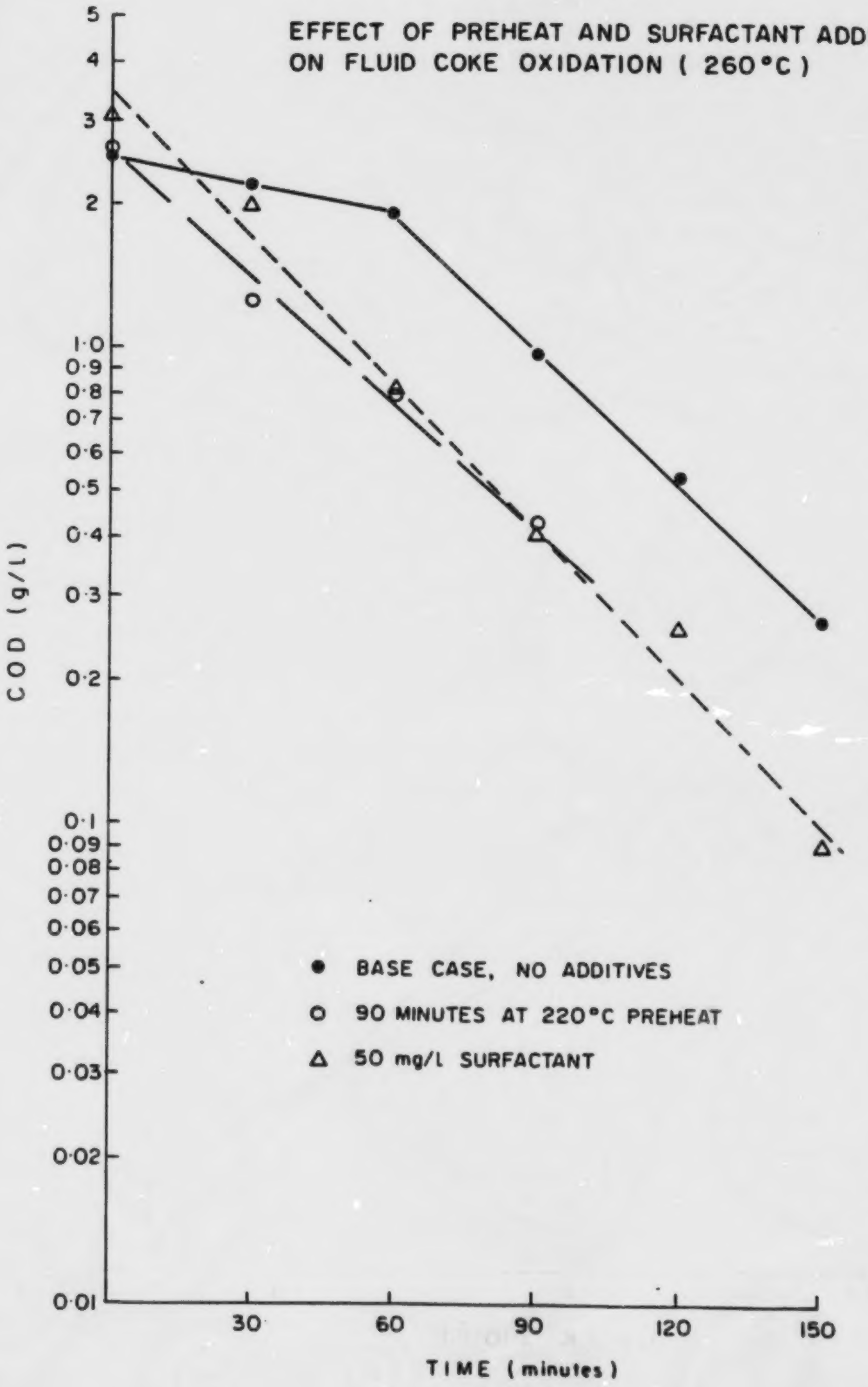


FIGURE 5·16

ARRHENIUS PLOT - FLUID COKE

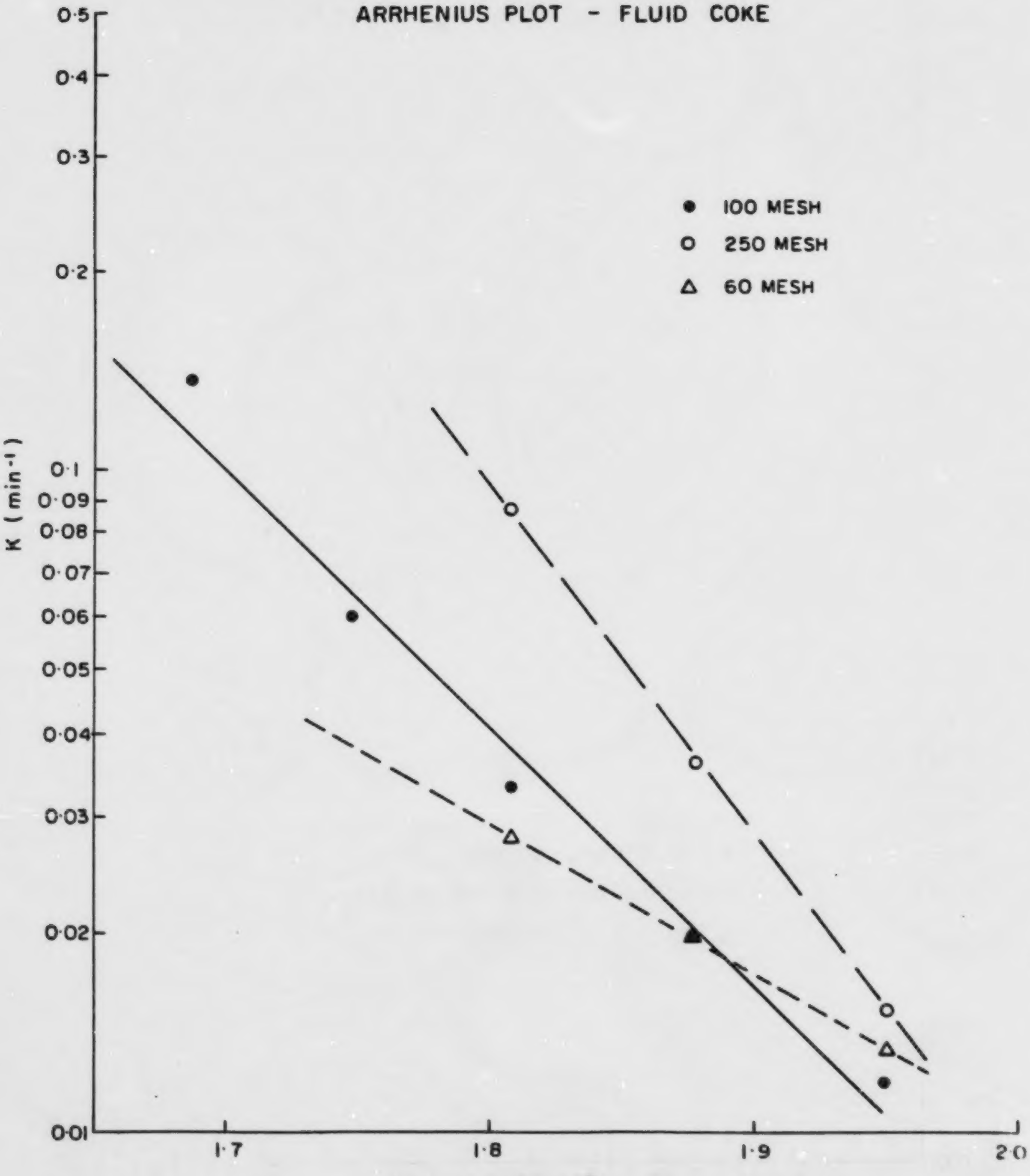


FIGURE 5.17

FLUID COKE - EFFECT OF O_2 PRESSURE

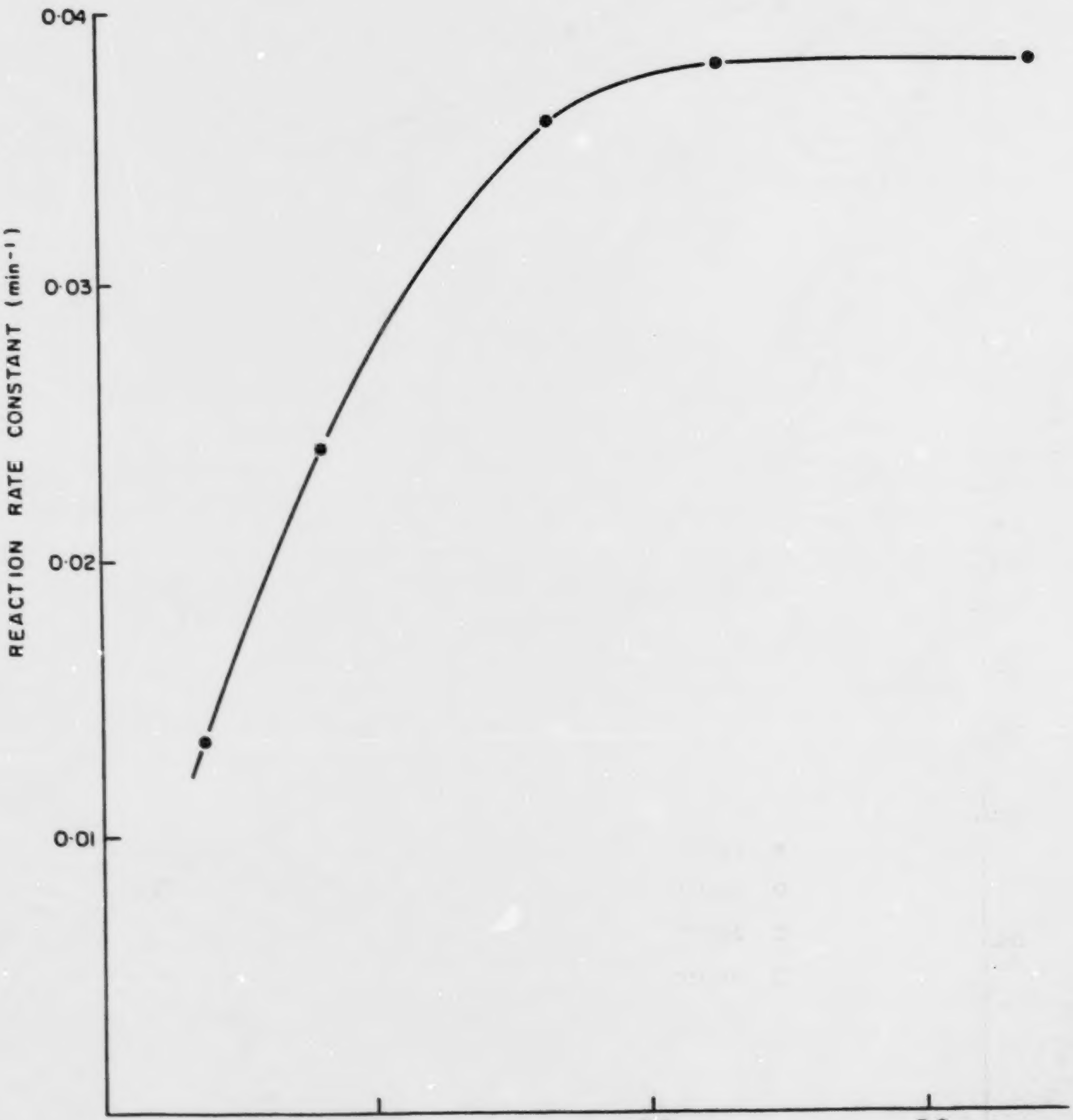


FIGURE 5.18
ATHABASCA PITCH KINETICS
NO ADDITIONS

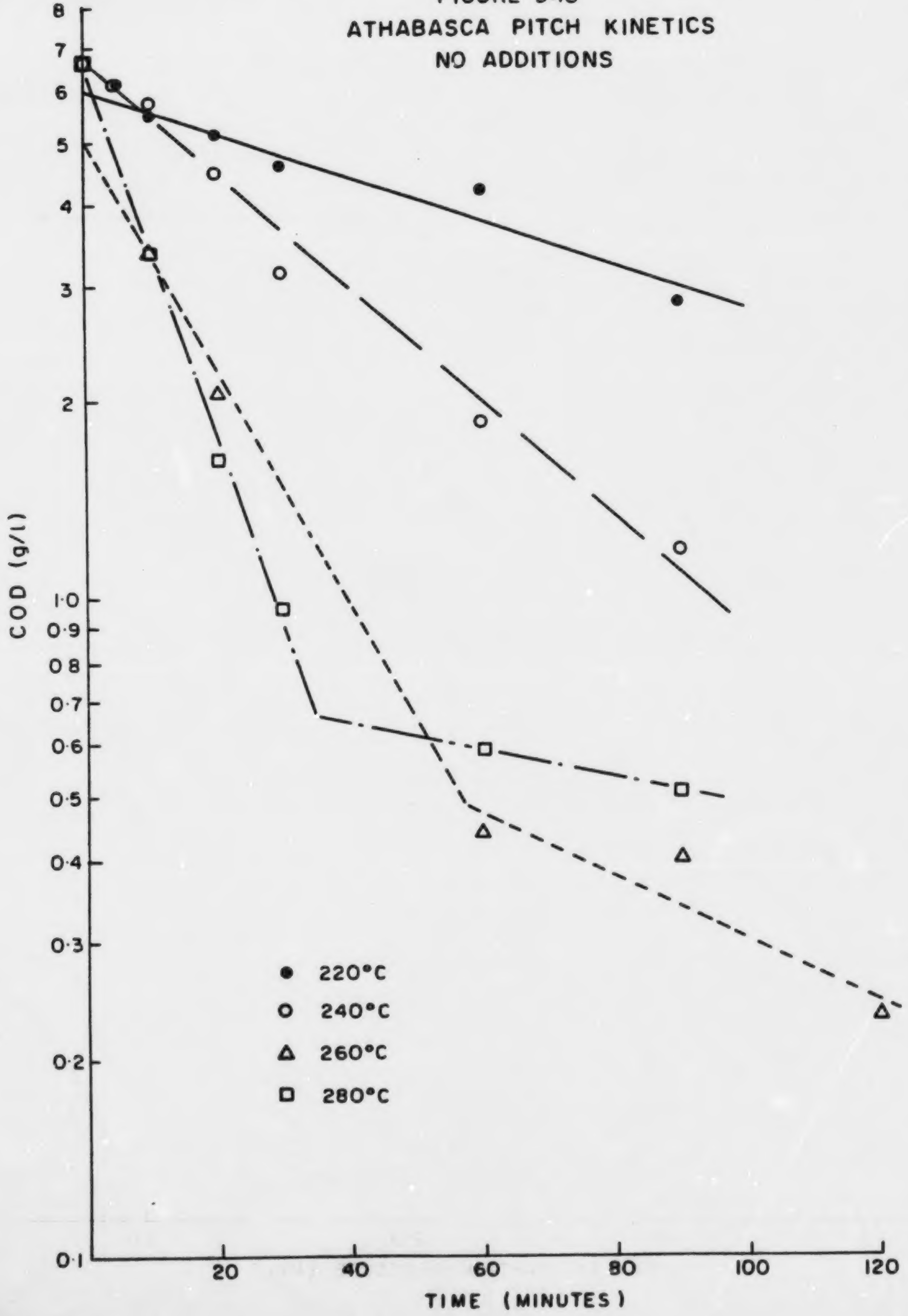


FIGURE 5.19

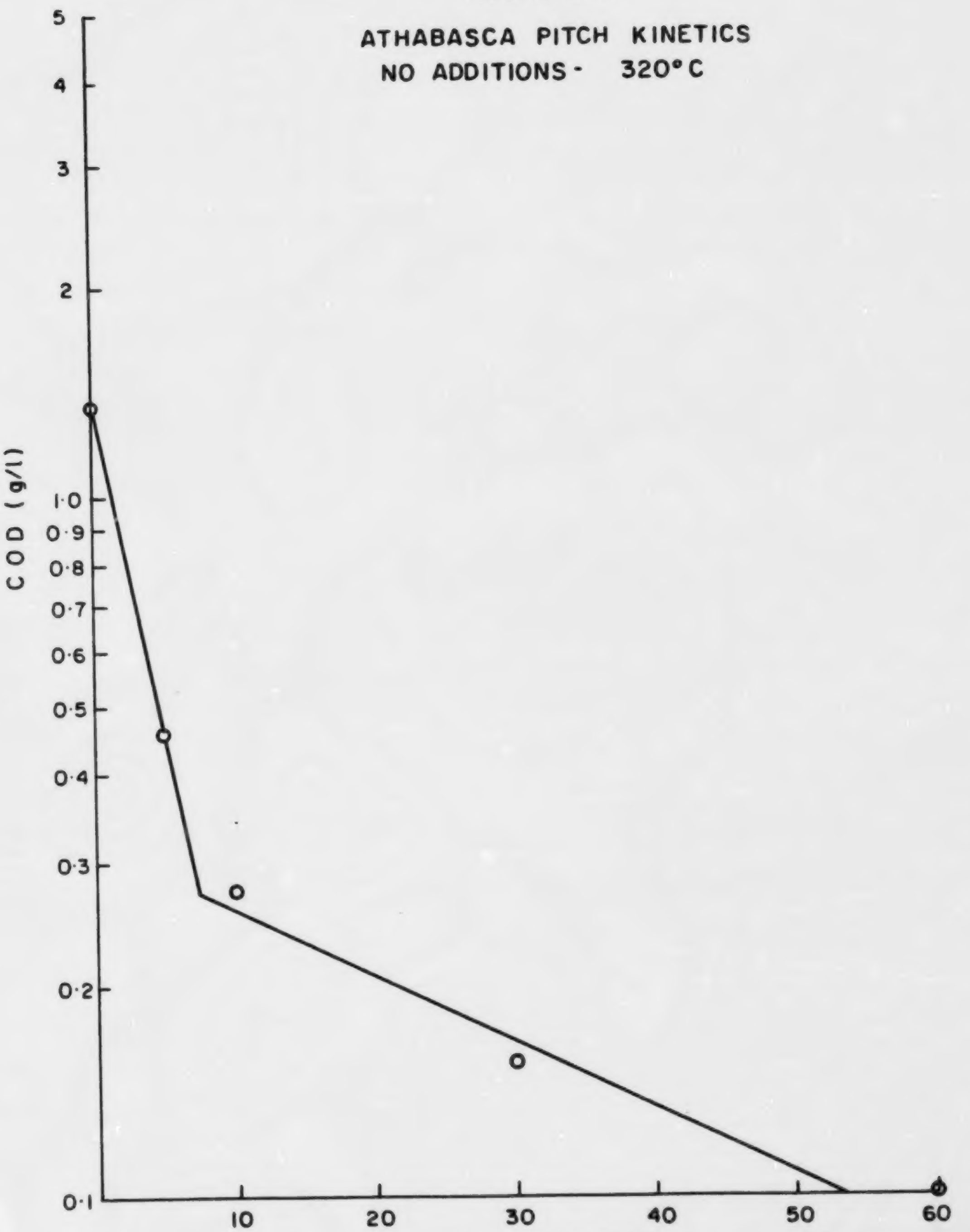

ATHABASCA PITCH KINETICS
NO ADDITIONS - 320°C
COD (g/l)
5
4
3
2
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
10
20
30
40
50
60
TIME (MINUTES)

FIGURE 5.20

ATHABASCA PITCH - ARRHENIUS PLOT

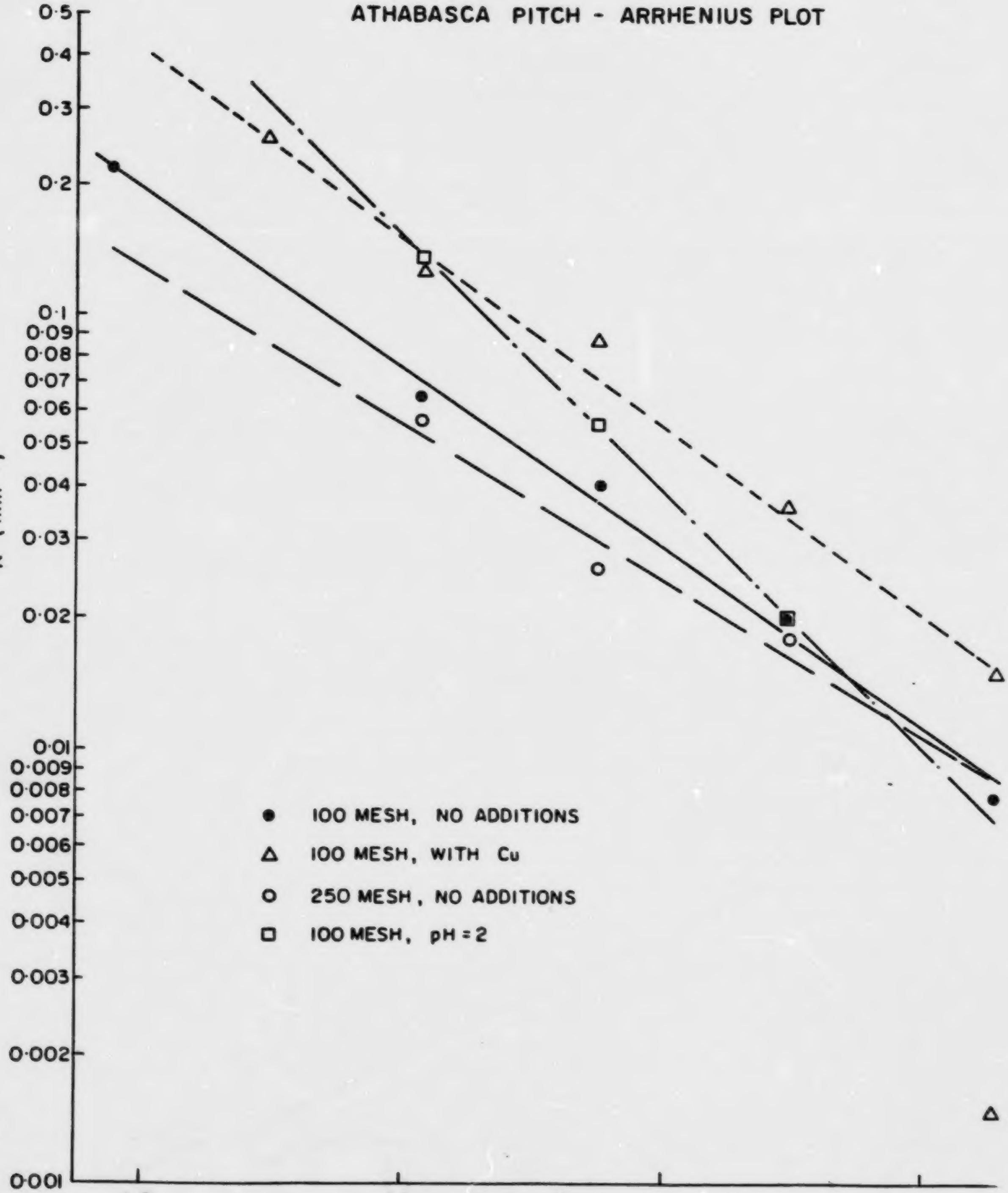


FIGURE 5.21

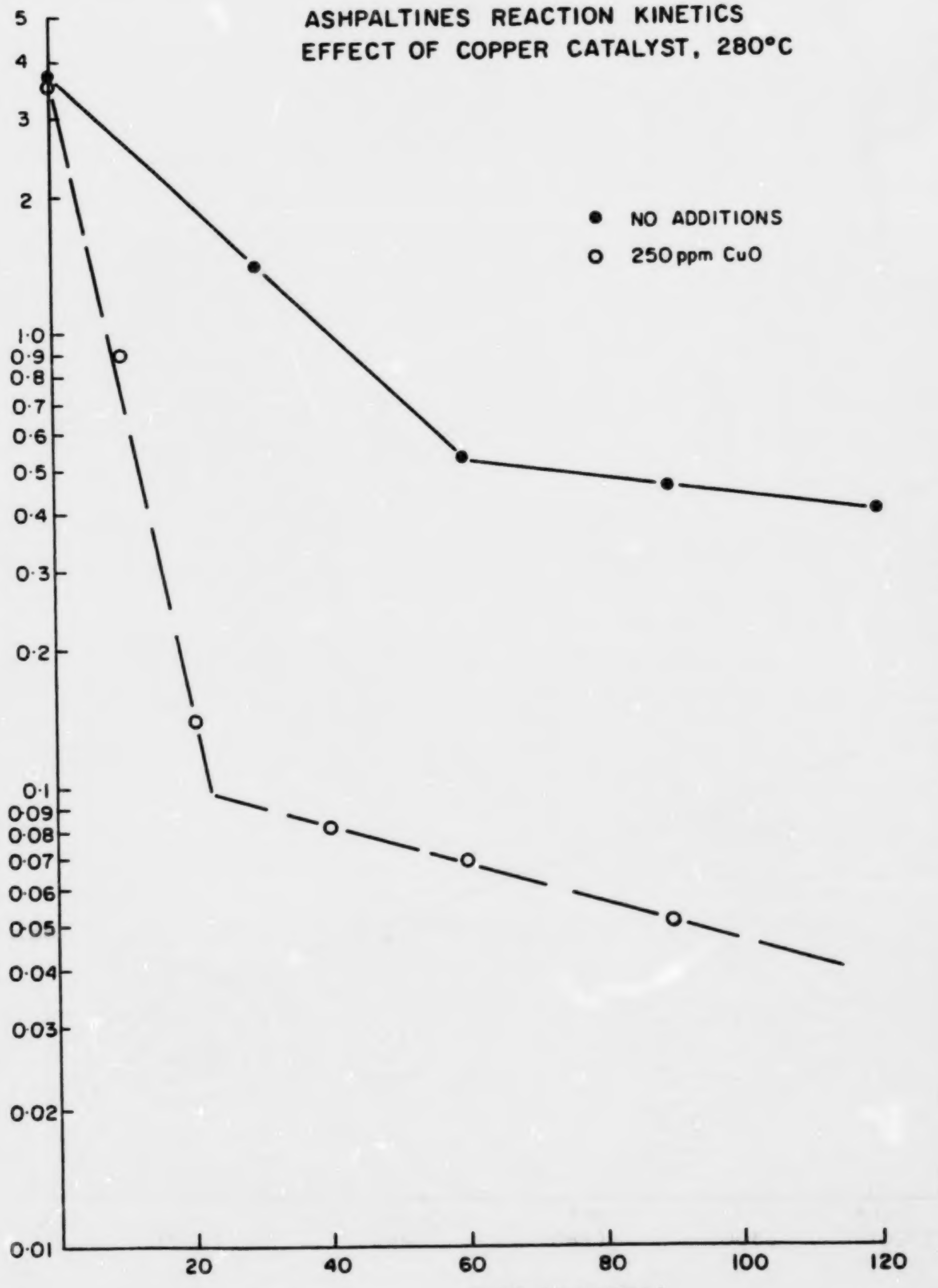

ASHPALTINES REACTION KINETICS
EFFECT OF COPPER CATALYST, 280°C
● NO ADDITIONS
○ 250ppm CuO
COD (g/l)
5
4
3
2
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·09
0·08
0·07
0·06
0·05
0·04
0·03
0·02
0·01
20
40
60
80
100
120
TIME (MINUTES)

FIGURE 5.22

ASPHALTINES ARRHENIUS

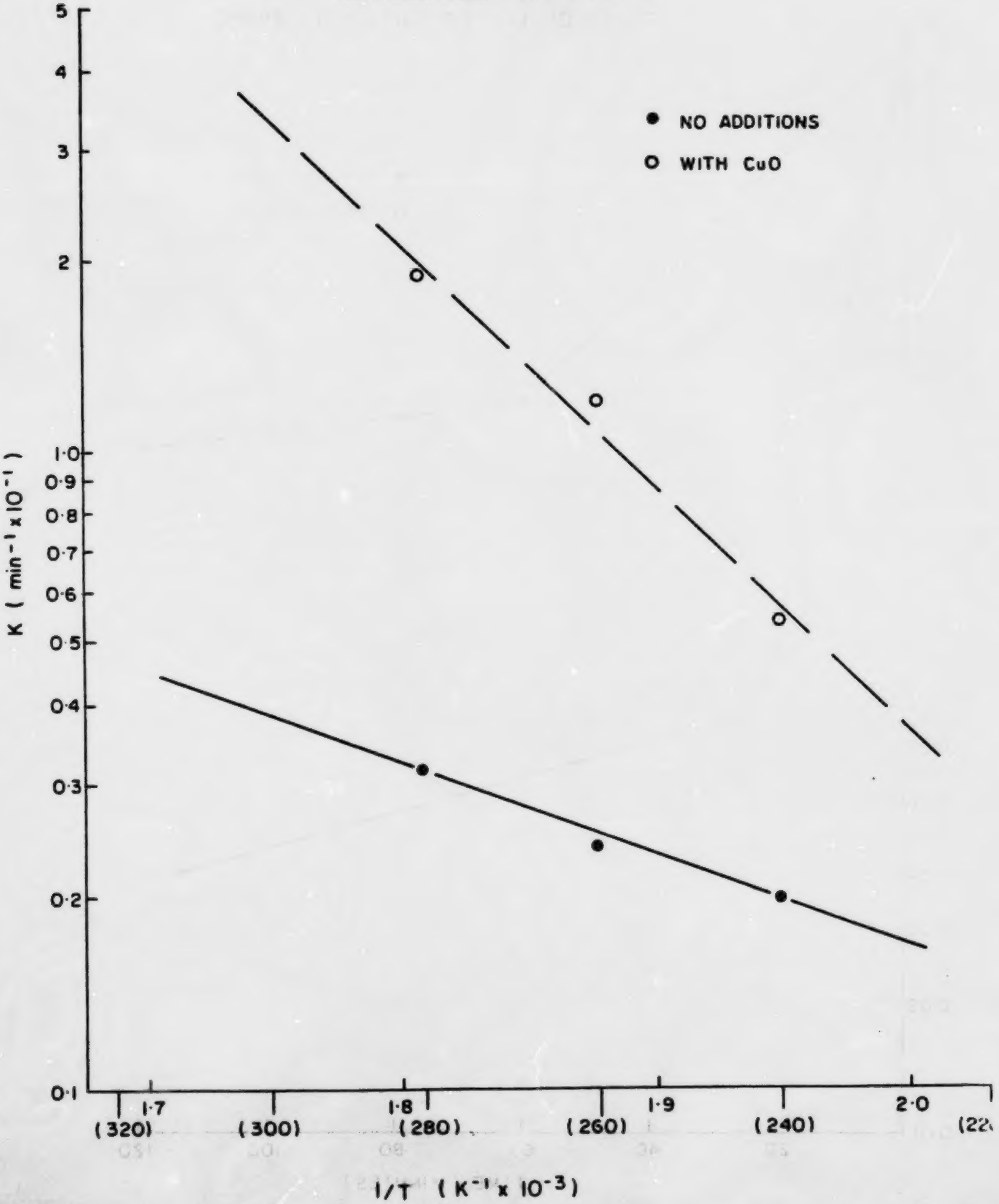
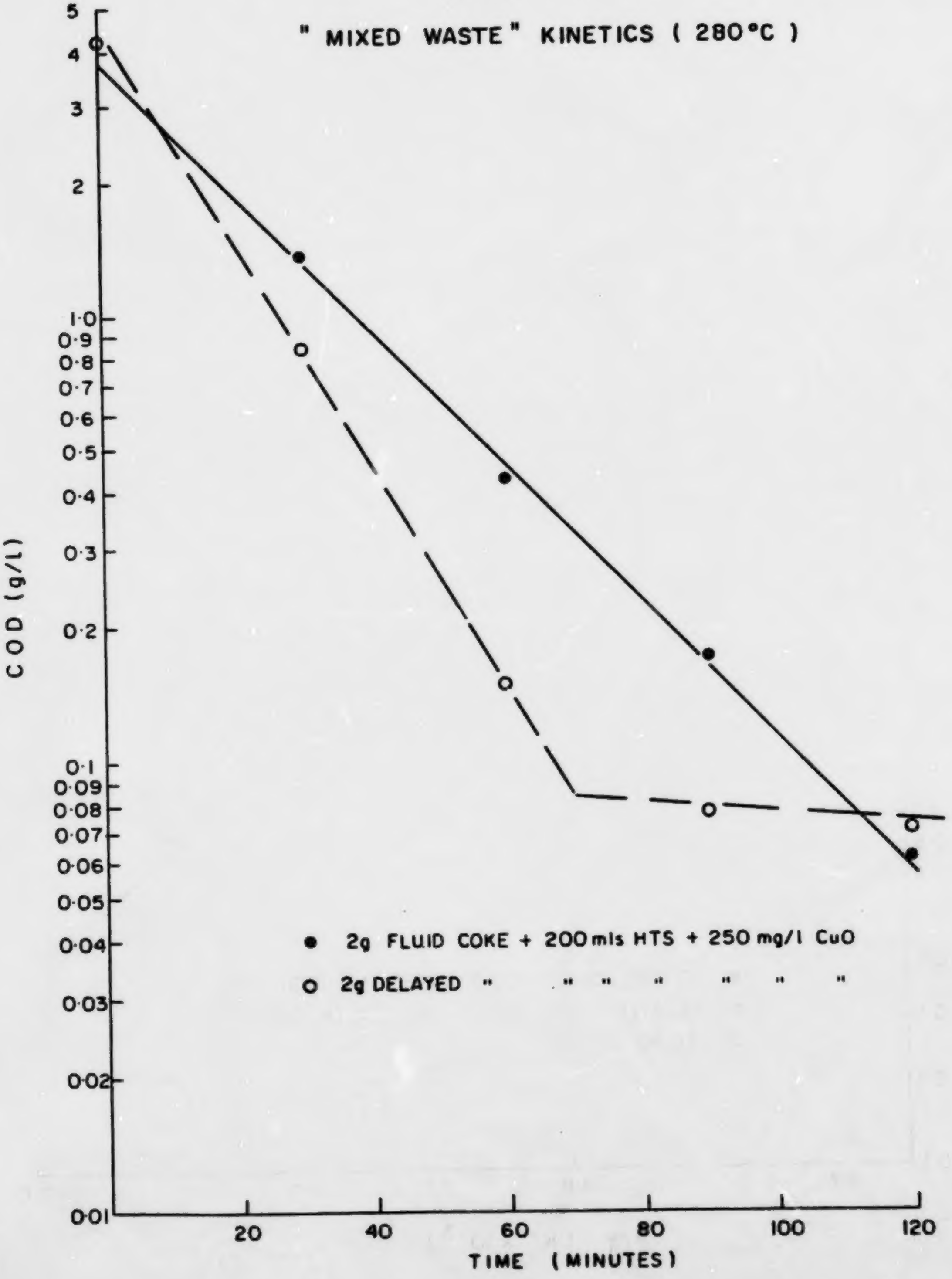


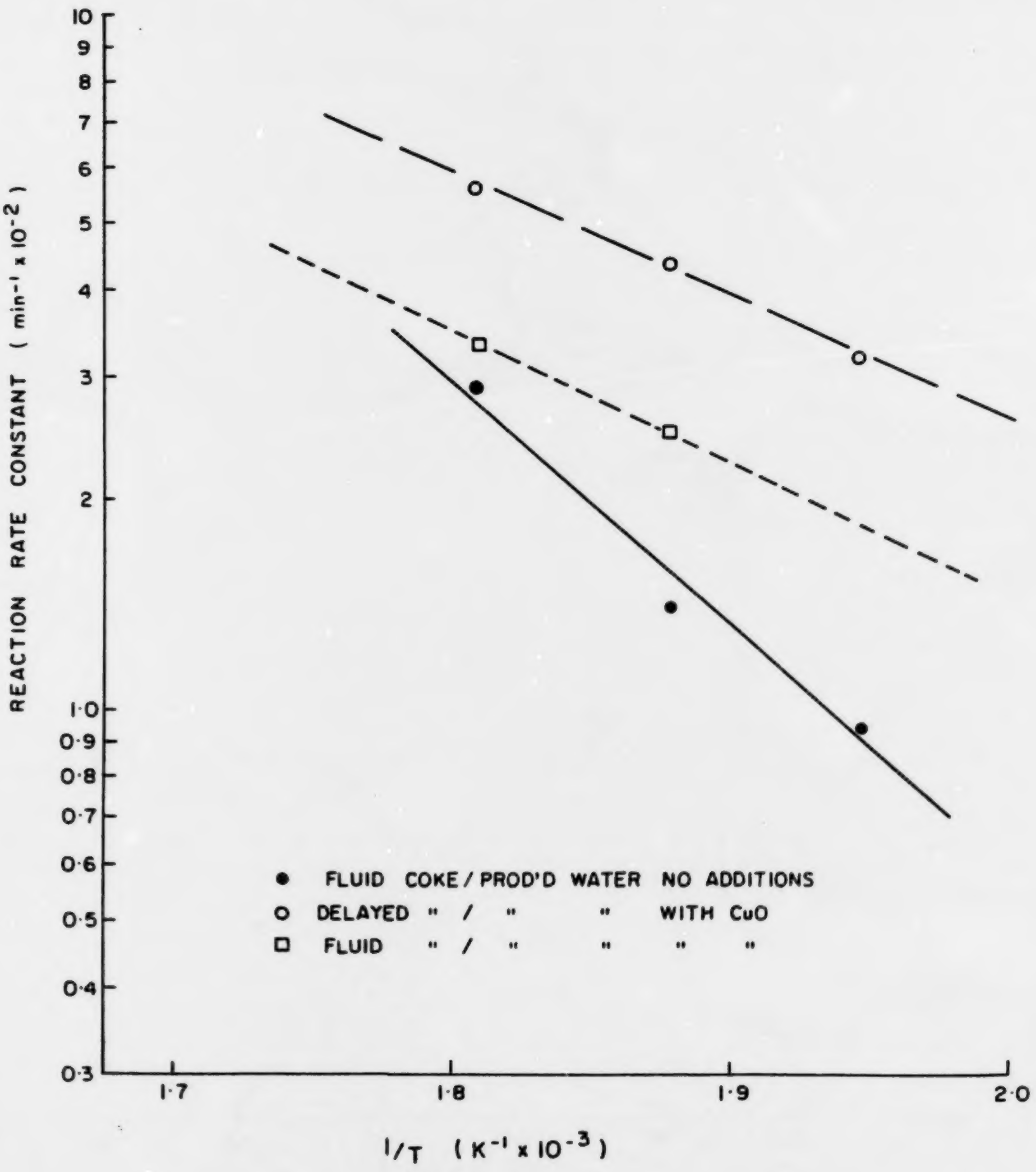
FIGURE 5.23



" MIXED WASTE " KINETICS (280°C)

FIGURE 5·24

" MIXED WASTE " ARRHENIUS



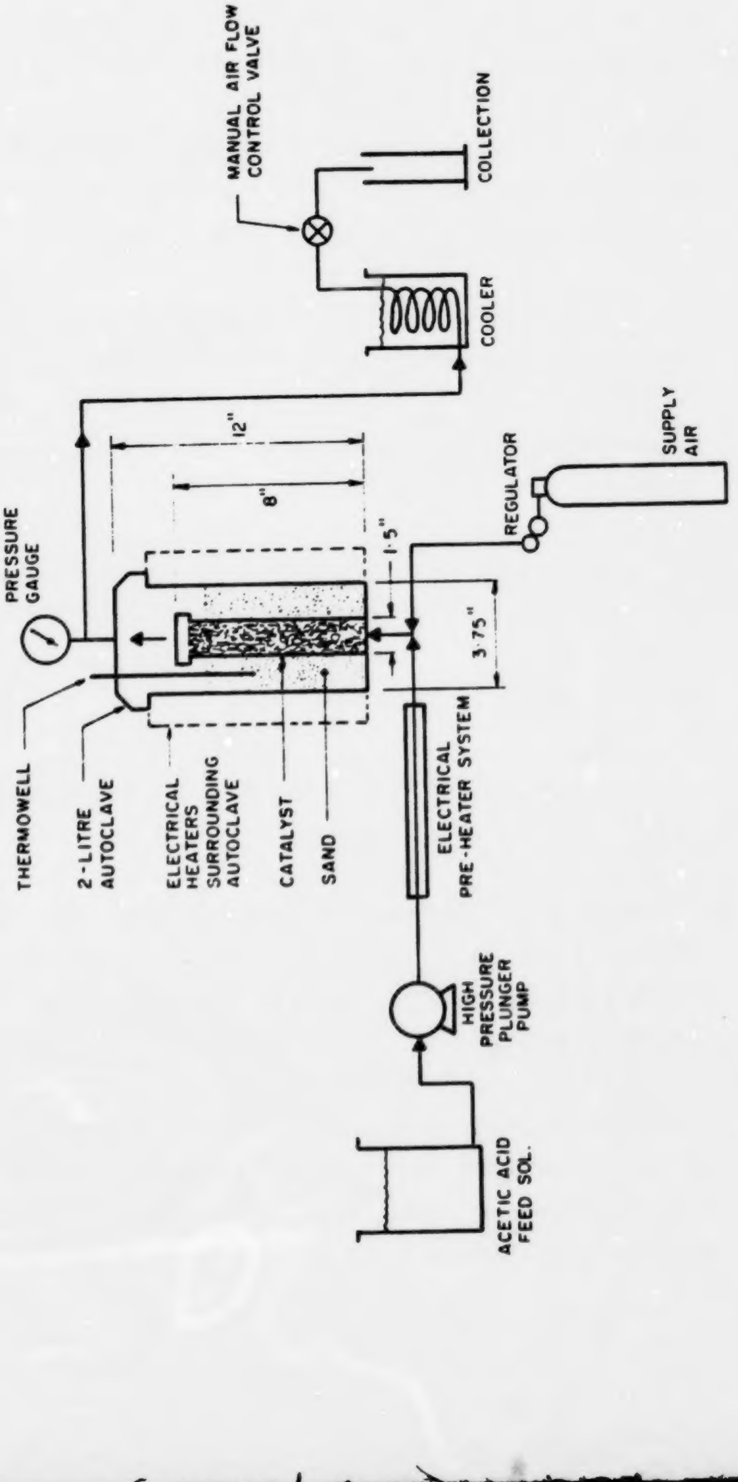

MANUAL AIR FLOW CONTROL VALVE
COLLECTION
COOLER
PRESSURE GAUGE
12"
8"
1·5"
3·75"
REGULATOR
SUPPLY AIR
THERMOWELL
2-LITRE AUTOCLAVE
ELECTRICAL HEATERS SURROUNDING AUTOCLAVE
CATALYST
SAND
ELECTRICAL PRE-HEATER SYSTEM
HIGH PRESSURE PLUNGER PUMP
ACETIC ACID FEED SOL.

FIGURE 5.25
VAPOUR PHASE CATALYSIS SYSTEM

6. PATENT - HIGH THERMAL FLUX WET OXIDATION STEAM GENERATOR

Wet air oxidation of low grade fuels has a number of important advantages over conventional dry incineration. These advantages include:

- Sulfur contained in the fuel is converted to sulfuric acid in wet oxidation, consequently eliminating costly flue gas desulfurization.

- The high ash content of many low grade fuels necessitates complex and problematic ash removal equipment in conventional boilers. In wet oxidation, the ash exits the reactor in a concentrated acidic liquid phase, and can often provide the potential for mineral recovery.

The major problem with the wet oxidation approach is that only very dilute fuel:water slurries can be tolerated due to physical-chemical equilibria within the unit. The net result, therefore, is low energy recovery per unit volume of reactor vessel.

There are two fundamental factors which govern the maximum concentration of fuel in the feed slurry:

1. Humidity Ratio: The mass of steam contained per unit mass of air is a function of temperature and total pressure. Knowing this ratio, and assuming a steam production rate, the air flowrate (and, hence, fuel concentration) can be calculated.

2. Energy Production: Basically, the energy entering and produced within the process cannot exceed the energy removed in the liquid and vapour effluents. If it does, the temperature of the reactor rises.

In the course of the present experimental program, a modification to the wet oxidation reactor was conceptualized, which would result in the humidity ratio alone governing the allowable fuel concentration. Therefore, by selective manipulation of process controllable variables (i.e. temperature, pressure), the specific fuel concentration can be increased.

Record of Invention No. 820 was filed at Ontario Research explaining the concept. As the idea was felt to merit protection, a Canadian Patent was subsequently applied for on January 30, 1985. The technology is currently owned by Canadian Patents and Development Ltd. (CPDL). A copy of the Patent Application is given in Appendix G.

6.1 Description of Invention

The obvious impact of increasing the fuel concentration is that the system heat output will correspondingly increase. If this quantity exceeds that which can be removed via the process vapour phase and liquid phase effluents, the temperature will increase. This invention allows for the removal of this excess energy, by simply installing heat recovery, or cooling coils, directly in the vessel.

The fundamentals of the invention are best explained by performing a thermodynamic comparison of the unmodified and modified systems for an example scenario. A simple flow diagram is given in Figure 6.1. The reaction temperature and total pressure were arbitrarily selected as:

$$T = 300^{\circ}C$$
$$P = 14\ \text{MPa}$$

The problem is to determine the solid fuel concentration allowable in the feed slurry, and, thus, the system heat output. (If the organic concentration is known, as in the case of many wet oxidation applications, the total reactor pressure is left as an unknown. Solving for total pressure, therefore, basically requires appropriate manipulation of the equations discussed in the following).

(i) Unmodified Wet Oxidation Reactor

As mentioned previously, the allowable fuel concentration is a function of the humidity ratio and process energy balances. These are defined and calculated as follows:

1. Humidity ratio:

$$HR = \frac{MW_w}{MW_g} \quad \frac{P_v}{P_T - P_v}$$

where: HR = humidity ratio (wt steam/wt gas)

MW_w, MW_g = molecular weight of water and oxidizing gas respectively

P_v = partial pressure of water vapour at temperature (MPa)

P_T = total confining pressure (MPa)

Therefore, at the specified conditions, and assuming air as oxidant, the HR becomes:

$$HR = 0.99 \, \frac{\text{kg steam}}{\text{kg air}}$$

and, assuming: 2.5 kg oxygen/kg solid fuel

0.2314 kg oxygen/kg air

the specific steam production rate to solid fuel flowrate ratio (steam/fuel) can be calculated:

$$\frac{\text{Steam}}{\text{Fuel}} = 0.99 \, \frac{\text{kg steam}}{\text{kg air}} \quad 0.2314 \, \frac{\text{kg } O_2}{\text{kg air}} \times 2.5 \, \frac{\text{kg } O_2}{\text{kg fuel}}$$

$$\text{Steam/fuel} = 10.7 \, \frac{\text{kg steam}}{\text{kg solid fuel}} \qquad (1)$$

2. Energy Balances (From Figure 6.1)

Feed Enthalpy + Heat of Combustion = VPE Enthalpy + LPE Enthalpy + Excess Energy

and, therefore:

$$m_f \times H_c \times e + m_F \times sh_L \times T_F = m_v \times sh_V + m_L \times T_R + H_E \qquad (2)$$

where: m_f = mass flowrate of fuel (kg/time)
H_c = heating value of fuel (MJ/kg)
e = oxidation efficiency
sh_L = specific heat of liquid (approx. 0.0044 MJ/kg/^{o}C)
m_F = mass flowrate of feed liquid (kg/time)
T_F = feed temperature (^{o}C)
m_V = mass flowrate of VPE (kg/time)
sh_V = specific heat of vapour (approx. 2.5 MJ/kg)
H_E = excess heat produced during reaction, which exceeds VPE + LPE removal limits
m_L = mass flowrate of LPE (kg/time)
T_R = reaction temperature (^{o}C)

Assuming that:

m_F = 100 kg/time
H_c = 35 MJ/kg
T_F = 50^{o}C
T_R = 300^{o}C
e = 0.9

$$m_L = m_f - m_V$$
$$H_E = 0$$

Substitution of the above into equation (2) reduces it to two unknowns:

$$31.5\ m_f = 1.18\ m_V + 110$$

or

$$31.5 = \frac{1.18\ m_V}{m_f} + \frac{110}{m_f} \qquad (3)$$

Substituting Equation (1) into equation (3), and solving:

m_f = 5.82% solid fuel
m_V = 62.4% of feed
m_L = 37.6% of feed

(ii) Modified Wet Oxidation Reactor

The steam/fuel ratio as calculated for the "normal" wet oxidation system is the same as for this case:

$$\frac{\text{Steam}}{\text{Fuel}} = 10.7\left(\frac{\text{kg steam}}{\text{kg solid fuel}}\right) \qquad (1)$$

The energy balance equation (2) is reproduced, with the additional unknown variable, H_E (excess heat generated):

$$31.5 = 1.18\ \frac{m_V}{m_f} + \frac{110}{m_f} + \frac{H_E}{m_f} \qquad (4)$$

It is apparent that the two equations (1) and (4) contain three unknown variables and, therefore, are indeterminant. However, assume that the vapour phase effluent is desired at 90% of the feed flowrate. Direct substitution into equation (1) gives:

$$\text{Solid fuel} = 8.41\%$$

Substituting into equation (3):

$$H_E = 48.7 \text{ MJ/time}$$

Therefore, to maintain reactor temperature and prevent a runaway reaction, 48.7 MJ per unit time must be removed from the unit.

6.2 Summary

The total heat output of this modified system is 294.4 MJ/unit time, compared to 203.7 MJ/unit time for the unmodified system. In other words, for a given system heat output, at identical reactor conditions, the modified reactor is approximately 45% smaller. Furthermore, the vapour production rate is considerably more for the modified system (90/62.4 approximately 44% greater). Therefore, because the wet oxidation reaction occurs only in the liquid phase, it is obvious that the greater the evaporation, the greater the hydraulic residence time in the unit. In conclusion, to realize an equal residence time between the two examples, the modified reactor system will be a further 44% smaller.

The overall impact of the invention becomes apparent. To realize the same heat output a modified vessel would have to be less than 20% of the size of a conventional unit. The coils, themselves, would occupy only a small volume within the unit, due to quite high heat transfer efficiencies which would be expected in the turbulent environment.

The energy recovered by the internal coils cannot be used as direct high pressure injection steam for in-situ oil recovery because the temperature (and, hence, vapour pressure) is too low. There are essentially two options for use of this steam in oil recovery operations:

1. Production of high temperature water (approximately 280^{o}C), which can be subsequently passed through a steam generator for high pressure steam production. Assuming 280^{o}C, and 80% quality injection steam desired, about 60% of the total enthalpy necessary is contained as sensible heat. Therefore, fossil fuel operating costs and steam generator size would be correspondingly decreased.

2. Production of low pressure (approximately 6.4 MPa) process steam for on-site electrical generation or heat requirements.

Consideration of these two alternatives is given in the Technical and Economic Assessment, Section 7.

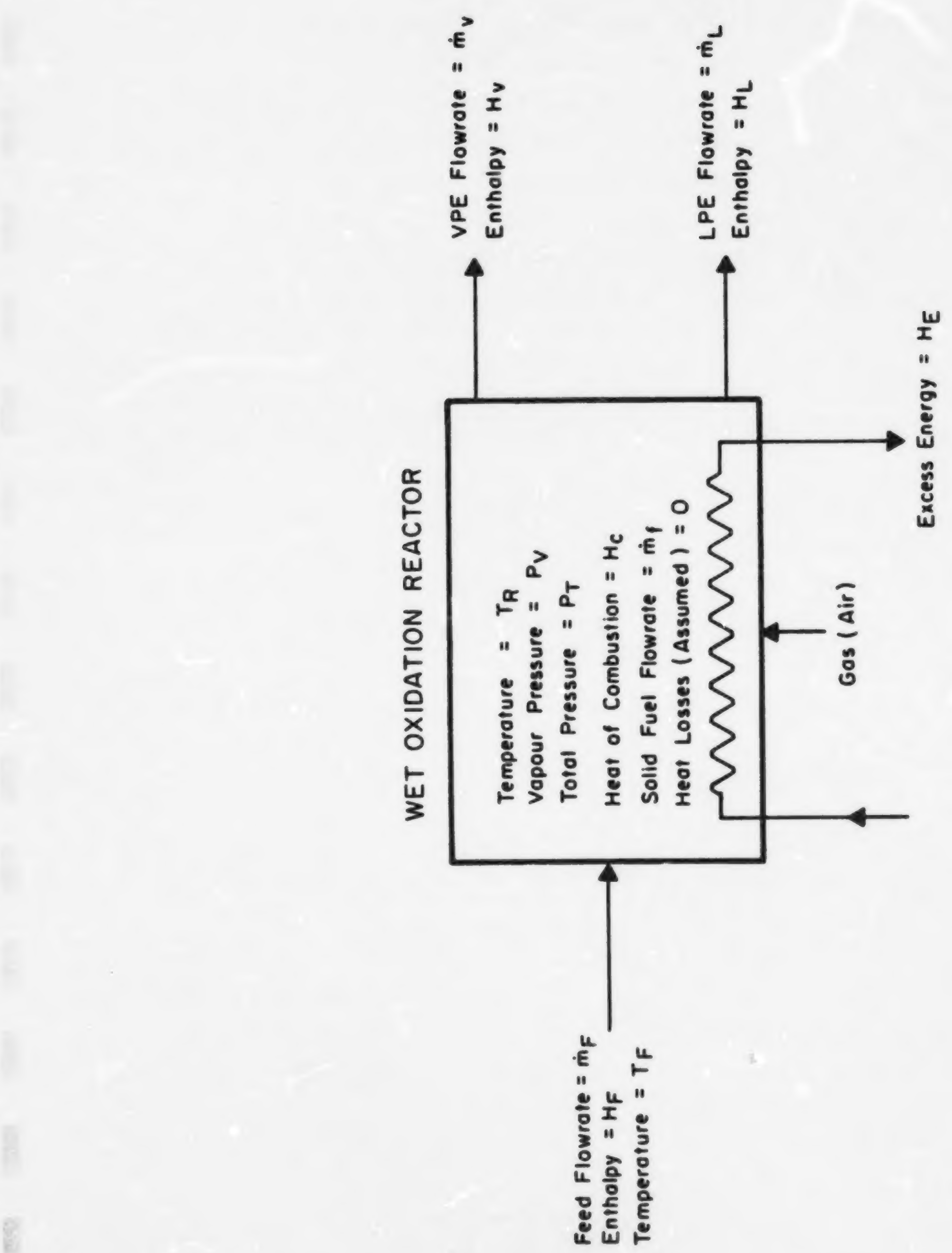

WET OXIDATION REACTOR
Temperature = T_R
Vapour Pressure = P_V
Total Pressure = P_T
Heat of Combustion = H_C
Solid Fuel Flowrate = $\dot{m}_f$
Heat Losses (Assumed) = 0
VPE Flowrate = $\dot{m}_V$
Enthalpy = H_V
LPE Flowrate = $\dot{m}_L$
Enthalpy = H_L
Excess Energy = H_E
Gas (Air)
Feed Flowrate = $\dot{m}_F$
Enthalpy = H_F
Temperature = T_F

FIGURE 6.1 MASS / ENERGY FLOW SCHEMATIC

7. TECHNICAL AND ECONOMIC ASSESSMENT

The results of the research conducted in this programme, and the patented modification to the Wetox process, has indicated that a considerable number of options are available for the application of wet oxidation in oil sand recovery operations. In order that the technical and economic significance of the many options be evaluated, a computer model, simulating the Wetox process was constructed. This model was written using the Microsoft(R) Fortran language (Microsoft Corporation). The computer employed was a Hyperion with 256 K random access memory.

A list of the 275 line program is given in Appendix G.

7.1 General Description

Six options were included in the program algorithm. The desired option is selected by simply changing the appropriate input variable. In addition, judicious use of the other 22 input variables permits minor modifications to the major options, as well as sensitivity to changes in materials of construction, solid fuel type, utilization and chemical costs, etc.

The program utilizes the reaction kinetics, specifically the Arrhenius parameters, which were determined during the current research. Only the first reaction regime is included, and it is assumed that this reaction proceeds until a desired destruction efficiency is realized. In effect, therefore, the model is most ideally suited to solid fuels, in which a second regime does not become apparent until 90-95% destruction is obtained. For cases in which a mixed solid fuel/produced water is used, it is best to assume the kinetics established for the solid fuel, because the produced water organic concentration, by comparison, will be small.

Finally, the potential modification to the Wetox process (Section 6) is included as part of the calculations. Therefore, system specifications are determined only by mass balances around the process. The energy output from the system is an input variable, which sets the mass flowrate of solid fuel feedstock. Based on the material flowrates, energy balances are constructed. If excess energy is produced which cannot be removed in the "normal" liquid and vapour effluents, heat recovery coils are installed into the reactor vessel per the patent description. If the energy balance, at certain conditions, is negative, natural gas is employed to supplement the system heat requirements.

There are six major options incorporated into the computer model. These are described briefly in the following, and are shown schematically in Figures 7.1 to 7.6.

Option 1: Air based Wetox system - A credit is given for the sum of the thermal energy value of the internal coil and LPE (liquid phase effluent) recovered as high temperature water. Cost of the vapour phase effluent (VPE) steam for direct oil well injection is calculated ($/GJ). Spent combustion gases (i.e. N_2, CO_2) are co-injected with the steam.

Option 2: Exactly the same as Option 1, except that a credit is given for sum of thermal energy value of the internal coil and LPE recovered as low pressure, process steam.

Option 3: Air based Wetox system - The total thermal energy output of the Wetox process is summed, and a cost of the energy ($/GJ) is calculated. Spent combustion gases are released to atmosphere. High temperature water or low pressure process steam could be the desired thermal energy product.

Option 4: Pure, cryogenic oxygen used as process oxidant. Relatively pure carbon dioxide is co-injected with steam. Otherwise, identical to Option 1.

Option 5: Pure cryogenic oxygen used as process oxidant. Otherwise, identical to Option 2.

Option 6: Pure cryogenic oxygen used as process oxidant. Similar to Option 3 in that the cost of the total thermal energy output as product is calculated. Provision is also available for giving a credit value for carbon dioxide (\$/kg). This may be applicable for in-situ oil recovery processes requiring "slug" injection of high pressure CO_2.

7.2 Input Variables

There are a total of 23 input variables. A description of each, along with the base case value, is given in the following:

Name	Description	Base Case Value
OXIDF	Oxygen concentration in feed gas. Included as an input variable mainly to account for the possible future inclusion of enriched air as oxidant, rather than strictly pure O_2 or air	1.0 or 0.2314 (wt/wt)
FF	Frequency factor	452,160 min^{-1}
EA	Activation Energy. Base case values of EA & FF from experimental data on fluid coke, no additions	17,927 cal/mole
R	Gas constant	1.99 cal K^{-1} $mole^{-1}$
CODRED	COD reduction. Specifies the desired extent of combustion	0.9
CN	Number of compartments in Wetox reactor	6
HEATOUT	System energy output	264,000 MJ/hr
RECEFF	Factor to account for heat losses and recovery efficiency from heat exchangers, etc.	0.95
AMATL	Material of construction. Three choices - Titanium, Grades 2, 7 or 12	12
DENS	Density of construction metal	4.5 g/cc
CCF	Factor to specify practical length of heat recovery cooling coils in Wetox reactor	1.0

CKWHR	Electricity cost	$0.03/kWhr
CF	Solid fuel cost. Base case value from Reference 1 and assuming heating value of 34.8 MJ/kg	$41.2/tonne
ALIME	Cost of limestone. Base case value from Reference 1	$45/tonne
ANAOM	Cost of sodium hydroxide. Base case value estimated from Chemical Marketing Reporter (19)	$300/tonne
CRF	Capital Recovery Factor. Base case value assuming 20 year plant life @ 15% interest	0.16
CH4	Cost of natural gas. Base case value from Reference 1	$0.0024/MJ
STM	Maximum VPE steam, or product hot water cost. This variable effectively limits the program output only to the most cost effective data sets	Varies with option selected
HW	Value to be credited for high temperature water (cost of natural gas + 46%)	$3.5/GJ
ST	Value to be credited for low pressure process steam (value of natural gas + 46%)	$3.5/GJ
CO2	Value to be credited for by-product carbon dioxide	$0.03/kg
OPT	Option selection	1 - 6
FMAX	Maximum feed solid fuel concentration deemed practical	0.3

7.3 Program Logic

The model is basically a parametric analysis, with three nested DO loops performing a series of calculations. The three DO loops, reaction temperature, pressure and vapour:feed ratio, are sufficient to allow the calculation of all mass and energy balances around the system.

A step by step general description of the operations undertaken during the program is given in the following:

1. External data files containing input variables are opened, read in and printed out.
2. Reactor temperature DO loop is initiated. Temperature starts at 260°C and increments by 10°C up to 320°C.
3. VPE:Feed rate ratio DO loop is initiated. Ratio varies from 0.5 to 0.9
4. Vapour pressure of liquid at temperature is calculated (MPa).
5. Minimum reactor pressure calculated based on vapour pressure plus required oxygen partial pressure defined during the test programme.
6. Reactor pressure DO loop initiated. Pressure incremented by 0.7 MPa for oxygen based system and 1.8 MPa for air based system.
7. Maximum reactor pressure set to 17.5 MPa (2540 psi). Cost analysis not believed to be applicable beyond this pressure.

8. Set minimum pressure to 13.8 MPa (2000 psi) if direct injection option is selected.

9. Calculate humidity ratio (kg steam/kg oxidant).

10. Calculate solid fuel concentration (kg fuel/kg liquid), assuming 2.5 kg O_2/kg coke required. If FMAX is exceeded, by-pass subsequent calculation.

11. Calculate reaction rate (min^{-1}) based on Arrhenius parameters.

12. Calculate COD remaining (wt/wt) at end of reaction based on input COD reduction.

13. Calculate required residence time for reaction (minutes) plus 10 minute safety margin. Batch scale reaction rate used, and transferred to continuous flow, multicompartment operation. Equation from Reference 20.

14. Calculate feed liquid flowrate (kg/min).

15. Calculate CO_2 production (kg/day).

16. Calculate reactor active volume with 20% safety margin (m^3).

17. Calculate reactor total volume (m^3).

18. Calculate reactor diameter (m). If diameter is greater than 1.7 m, increase the number of reactors by one. This stipulation was made because only magnetic drive agitators were considered for the system, and, at present, the maximum capability of these agitators correspond to approximately 1.7 m.

19. Calculate reactor length (m), number compartments x diameter

20. Clad type fabricated vessel is employed. Calculate wall thickness (cm) and weight of carbon steel shell (kg).

21. Calculate fabricated cost of carbon steel shell ($).

22. Conduct energy balances based on calculated material flows (MJ/min). Calculate excess energy which must be removed using cooling coils (if positive) or supplemental energy required (if negative).

23. Calculate cooling water flow required to remove excess heat, assuming vaporization of water (kg/min/reactor).

24. Calculate coil specification for first compartment (coil will be largest in the first compartment).

25. Add the volume occupied by coil to the reactor volume. If coil volume is greater than 10% of total volume, return and calculate new set of reactor size specifications.

26. Calculate cost of natural gas if energy balance is negative ($).

27. Calculate length of coil deemed practical in the first compartment of the Wetox reactor (m). Two nested coils are assumed maximum for the base case condition. An input constant can be employed to increase or decrease size as desired.

28. Calculate oxygen flowrate (kg/min).

29. Calculate oxidant flowrate (L/min).

30. Calculate compressor energy requirement (hp and kw).

31. Calculate capital cost of Wetox reactor ($). The cost of the clad vessel is conservatively estimated at fabricated cost of carbon steel shell, plus 1.25 cm titanium cladding ($/kg). The normal clad thickness is about 0.5 cm. The greater thickness assumed accounts for additional fabrication labour required (per discussions with Titanium Co., Montreal, Canada)(17).

32. Calculate cost of agitators assuming 18% (Grade 7) to 20% (Grade 2, 12) ($).

33. Calculate cost of compressor (based on horsepower size), heat exchangers (10-30 percent of reactor cost, dependent on the option selected) and pump (flowrate-pressure multiplier).

34. Calculate major equipment costs. Sum of reactor, heat exchangers, pump, compressor and agitators.

35. Calculate balance of plant items based on percentages of major equipment cost. Plant components are as follows:

Installation = 25% (of Major Equipment)
Piping = 12% (of Major Equipment)
Insulation = 3% (of Major Equipment)
Controls = 13% (of Major Equipment)
Electrical = 10% (of Major Equipment)
Engineering = 5% (of Major Equipment)
Miscellaneous = 7% (of Major Equipment)
Contingency = 25% (of Major Equipment)

36. Calculate total plant capital, and annualize based on selected capital recovery factor.

37. Calculate capital and operating cost for oxygen plant, if oxygen based system selected. Equation from Shreve & Brink(21), scaled to 1984 using chemical engineering cost indices.

38. Calculate plant operating costs (assuming 330 days/year operation):

Labour:	Assumed insensitive to economics of scale. 2 operators per shift; 3 shifts per day; 365 days per year; $25/hr including overhead.
Fuel:	Cost obtained from Reference 1. Input variation set at $41.2/tonne for coke from Syncrude or Suncor plants.
Electricity:	Cost per kWhr is input variable. Base case set at $0.03/kWhr. Total power required assumed to be 10% greater than the huge gas compressor duty.
Maintenance:	Assumed to be 4% of total plant cost.
Chemicals:	Neutralization chemicals. Assumed 25% required using sodium hydroxide, and 75% using limestone. This allows feeding caustic into the reactor to minimize corrosivity. Fuel sulfur assumed to be 7%.

Waste Treatment:

Solids disposal only considered. Basically includes ash contained in the solid fuel and gypsum generated by neutralization. Sludge assumed to be 70% moisture. Trucked to landfill at $10/tonne.

39. Calculate total annual operating costs. Include negative costs for credits for coil and LPE energy and carbon dioxide, if appropriate option selected.

40. If direct injection type system, calculate energy exiting system in the vapour phase effluent.

41. Calculate steam cost. If greater than input variable (STM), by-pass subsequent output statements.

42. Calculate hot water cost. If greater than input variable (STM) by-pass subsequent output statements.

43. Write the desired output information.

44. Increment reactor pressure.

45. Terminate pressure, vapour:feed ratio and temperature DO loops

7.4 Output Description

Twenty variables are included with each "family" of results. The number of families can be as great as 175, if the various manually imposed limits on the program output are adjusted appropriately. However, it is preferable to minimize each output to ease the task of organizing the results.

Each output set of results includes the following information:

- Reactor temperature (^{o}C)
- Reactor pressure (MPa)
- VPE/feed ratio (wt/wt)
- Solid fuel concentration in feed (wt/wt)
- Number of reactors
- Total volume of each reactor (m^3)
- Feed rate into each reactor (kg or L/min)
- Vessel diameter x vessel length (m x m)
- Compartment #1 cooling coil diameter x length (cm x m)
- Volume occupied by cooling coil (m^3)
- Water flow through cooling coil (L/min)
- Cooling coil heat output (MJ/hr)
- Vapour phase effluent steam (MJ/hr)
- Liquid phase heat output (MJ/hr)
- Oxygen plant capital cost ($)
- Annual operating costs ($/yr)
- Annual capital costs ($/yr)
- Total capital cost ($)
- Thermal energy cost ($/GJ) Option 3, 6
- VPE steam cost ($/GJ) Option 1, 2, 4, 5

A conditional statement is included as part of the program output. If the cooling coil length is calculated to exceed that which is deemed practical, the following will be printed:

```
Practical coil length is only ...... m
```

This provision permits the user to make discretionary decisions regarding the length of coil, with due regard to the economics of the data set. In other words, if a particular set of conditions appears particularly cost effective, a more rigorous analysis of the cooling coil length would be justified.

7.5 Results of Computer Evaluation

With a total of six possible options incorporated into the computer model, plus four sensitivity analysis, a considerable quantity of data has been generated. Therefore, the actual printouts containing the data sets for the base case conditions only are appended to this report (Appendix I).

In this section, a table is presented for each option listing the base case conditions causing the five lowest product costs. The base case input variables were given earlier in Section 7.2. In addition, a second table is presented for Options 1, 3, 4 and 6, for which scenarios a sensitivity analysis was conducted.

The respective tables for all cases are given in the following:

	Base Case	Sensitivity Analysis
Option 1	7.1	7.2
Option 2	7.3	Not done
Option 3	7.4	7.5
Option 4	7.6	7.7
Option 5	7.8	Not done
Option 6	7.9	7.10

7.6 Economic Analysis Discussion

The major purpose of this technical and economic assessment was to evaluate a number of different wet oxidation scenarios which may be applicable in oil sands recovery operations. Employing a computerized model allowed this task to be performed quickly and relatively easily. Furthermore, this model is currently constructed so that, in the future, more reliable cost information can be included as the development of the Wetox process in this application advances. At present, it is believed that calculated operating, capital and product costs are accurate to within ± 25%.

7.6.1 High Pressure Direct Injection Steam

Options 1, 2, 4 and 5 are constructed to model specifically the application of wet oxidation in in-situ steam stimulation type oil recovery operations. If one of these options is selected, a cost for high pressure steam for direct injection from the Wetox process itself into an oil bearing formation is calculated.

The computer model was constructed with future possible modifications considered. Only minor differences presently exist between Options 1 and 2, and between Options 4 and 5. In 1 and 4, a credit is given for high temperature water, which is created by heat exchange with the internal coils' working fluid (assumed steam for maximum heat transfer). A future addition to these scenarios would be to include a once through steam generator installed to accept this high temperature water for high pressure steam raising.

Options 2 and 5, on the other hand, utilize the coil working fluid itself, if low pressure process steam is desirable. Again, a possible future modification could include the addition of a steam turbine with generator for on-site electrical production.

The VPE steam costs calculated for the base case conditions indicate that an air based Wetox system is more cost effective than a pure oxygen system. Quantitatively, the VPE steam costs for the oxygen system are $2.40/GJ or 39% greater than that for the air system. The major reason for this fairly substantial cost differential is due to the system's complex mass and energy balances. Schematics of the balances are given in Figures 7.7 and 7.8 for Option 1 and Option 4 respectively, for the reactor conditions which resulted in the lowest product cost.

The gas flow for the air based system is about 5 times greater than that for the oxygen based process for a given "oxygen demand" in the Wetox process. Because of the humidity relationship, which expresses the steam production as a direct function of gas flowrate, more energy, or steam, is contained in the outgoing VPE in the case of the air process. Therefore, less energy is contained in the total of the "coil" fluid plus LPE effluents. In the base case model, these energy by-products have been assigned a low value ($3.5/GJ), as compared to the cost of the VPE steam, which effectively means that the optimum cost scenario would tend to occur at high VPE flowrates. Comparing Options 1 and 4, (Figures 7.7 and 7.8 respectively), it is apparent that the by-product energy accounts for approximately 24% of the total output energy for the air system and approximately 58% for the oxygen based process.

If the reaction temperature was allowed to be greater than 320^{o}C for the oxygen system, then the by-product energy credits (e.g. LPE + coil), as a fraction of the total Wetox energy output, would decrease. This can again be explained on the basis of the absolute humidity ratio. As the temperature rises, the water vapour pressure increases relative to the reactor pressure which, therefore, results in an increase in the capacity of the gas for water vapour.

In this computer model, the reactor temperature was limited to 320°C. This was instituted because titanium as a construction material is normally not suitable beyond this level. If future corrosion studies, in fact, indicate an alternative material may be suitable, then higher reaction temperatures may be employed, which would, undoubtedly, reduce the cost of VPE steam from an oxygen based system.

A further factor which complicates the comparison between the oxygen and air based Wetox systems is the allowable fuel concentration. This variable is calculated as follows:

$$FC = \frac{VPFR}{HR \times 2.5} \times O_2 \text{ Conc.}$$

where:
FC = fuel concentration (wt/wt)
HR = humidity ratio (wt steam/wt gas)
VPFR = VPE/feed ratio
O_2 Conc. = oxygen concentration in feed gas (wt/wt)

It can be seen that, at identical conditions (viz. temperature, pressure, VPE/feed ratio), the allowable fuel concentration in an oxygen based system is approximately 4.3 times greater than for an air based system. This effectively allows a smaller reactor system to be employed for a given energy output.

Although the foregoing discussion indicates that many interrelated factors influence the ultimate VPE steam cost for the oxygen and air based Wetox system, it must be emphasized that the costs do not reflect the desirability of the product. For example, it may not be a practical option to inject large volumes of nitrogen along with the combustion gases into the oil well. In the case of an oxygen system, almost pure carbon dioxide would be injected with the steam, and a credit may be justified. More insight into the oxygen versus air debate is given in Section 8.

The four most sensitive variables subjected to a sensitivity analysis for the high pressure steam options were:

- System heat output (MJ/hr)
- Solid fuel cost ($/tonne)
- Electricity cost ($/kWhr)
- Internal coil product credit ($/GJ)

The impact of these variables on the VPE steam cost is shown graphically in Figures 7.9 and 7.10 for Options 1 and 4 respectively. Electricity and fuel costs are seen to be critically sensitive variables, with the VPE steam costs increasing essentially linearily with variable changes over the range studied.

As expected, system heat output was not extremely sensitive around or above the base case value. At lower heat outputs (i.e. less than 100,000 MJ/hr) more rapid increases in product costs would be apparent.

Another critically sensitive variable seemed to be the credit given for the coil + LPE, thermal energy by-product (in Options 1 and 4, high temperature water is the desired by-product). In Option 1, the relationship between the variables change and VPE cost is not linear. At by-product credit values lower than the base case, little change in product cost is observed. Increasing the value of the coil + LPE credit to greater than the base case value, however, effects substantial VPE steam cost reductions. Assuming the credit for high temperature water was $5.5/GJ, for example, a VPE steam cost of $4.09/GJ would be realized.

7.6.2 Thermal Energy Recovery Systems

The product in Options 3 and 6 is measured as total recoverable thermal energy from the Wetox process. In essence, the "product" is the thermal energy value of the sum of:

- VPE steam, heat exchanged to produce either low pressure, process steam or high temperature water.
- LPE, heat exchanged to produce low pressure process steam, or high temperature water.
- Internal reactor cooling coil. If high temperature water is desired, a heat exchanger would be employed with the coil working fluid. Low pressure steam as desired product would not require this additional heat exchange network.

These scenarios would have application in oil sand mining complexes, in-situ recovery operations, or essentially any industry which would benefit from the use of low grade solid fuels in place of more conventional fossil fuels (e.g. natural gas, oil). It is assumed, of course, that low grade fuels, particularly upgrader residues, will have an inherently low cost exclusive of transportation costs.

The reactor temperatures resulting in the lowest thermal energy costs are significantly lower than those determined for the high pressure injection steam type systems. Furthermore, overall energy costs are less.

Mass and energy balances around the Wetox process are presented in Figures 7.11 and 7.12 for Options 3 and 6 respectively. Only the lowest product cost scenarios are given.

Even though the thermal energy costs were calculated to be lower than the VPE steam costs, comparisons may be misleading. For example, consider Options 1 and 3. The thermal energy cost was found to be \$5.06/GJ. If this appears to be a realistic price for high temperature water or low pressure process steam, then this should be used as the credit value for the coil + LPE energy by-product in Option 1.

Applying this credit to the sensitivity analysis for Option 1 (Figure.7.9), it can be seen that the VPE steam cost would be reduced to approximately \$5.00/GJ.

A three variable sensitivity analysis was performed on Option 3. The effect of changes in fuel cost, electricity cost and heat output on the thermal energy cost is given in Figure 7.13. A similar pattern is observed for this option as compared to the VPE steam option. Electricity cost does, however, appear to have slightly less impact on the thermal energy cost, probably due to lower reactor pressure (and, hence, compression energy) for Option 3.

The effects on the thermal energy cost due to changes in variables mentioned above, plus the carbon dioxide value credit, are shown in the sensitivity analysis for Option 6 (Figure 7.14). The most sensitive variable was determined to be the credit given to by-product carbon dioxide. It can be seen that, if this value were doubled from the base case value of \$0.03/kg (\$0.057/m^3 or \$1.61/Mcf), the thermal energy "product" would be essentially free.

7.6.3 Technical and Economic Assessment Summary

Applying the knowledge gained in this research program, and the use of a computerized technical and economic model, has resulted in a considerable array of possibilities for application of the Wetox process in oil sand recovery operations. The recent patented modification to the Wetox process has effectively reduced the size of the unit for a given energy output. It follows then that the actual cost of the energy, whether high pressure injection steam, or high temperature water/low pressure process steam, is lower when the internal heat reovery coils are employed. This point has been confirmed during the economic assessment. Even though reactor conditions would be encountered during the computer calculations which would result in no requirements for internal coils, none of these possibilities were included in the most cost effective data sets.

The economic significance of the heat recovery coil concept is more pronounced when the thermal energy product is selected instead of the VPE steam as product. Examining the mass and energy balances for Options 1 and 3, (Figures 7.7 and 7.11 respectively), it can be seen that approximately 20% of the total system energy output is contributed by the coils for Option 1 and about approximately 62% in the case of Option 3.

It can be seen in the base case cost summary tables that, in many of the Options, the calculated actual coil length has exceeded the "practical coil length". At this point in time, it must be emphasized, however, that neither of these calculated lengths is rigid. The practical coil length has been arbitrarilly set at 2 circumferenced coils, at appropriate spacing, placed in the first compartment of the Wetox reactor. An input variable is provided which can be changed to increase or decrease this length if desired. In actual practice, it is likely that this preliminary estimate of practical length is conservative, and can probably be exceeded. This will have to be confirmed as the development of the Wetox process continues.

Another item which would have to be confirmed in pilot scale development in the heat transfer coefficient in the internal coils. An extremely conservative value of 10.2 J/min-cm^2.^{o}C (300 Btu/hr/ft^2/^{o}F) was employed in the current model. At the turbulent and boiling conditions present in the Wetox reactor, it is probable that this value could be reasonably doubled. If this were, indeed, possible, few of the most cost effective options would be subject to an internal coil length limitation.

The computer model did not allow a credit to be given for water treatment or purification to liquid exiting the VPE of the Wetox reactor. In actual fact, the VPE would be effectively distilled, and, therefore, contain no dissolved or suspended solids. If a vapour phase catalytic system is not employed, particularly for produced water treatment, the VPE may contain residual organic species (e.g. volatilized hydrocarbons, oxidation by-products) as well as oxygen not consumed during reaction.

Similarly, a cost was not charged for boiler feedwater quality water required by the system's internal heat recovery coils. However, the base case credit value of this by-product ($3.5/GJ) was determined solely on the basis of equivalent natural gas energy cost plus a suitable margin for equipment and operating cost (e.g. $2.4/GJ for natural gas + $1.1/GJ for associated costs).

The most sensitive variables were found to be, in order of significance:

- Credit given to carbon dioxide (Option 6)
- Credit given to coil + LPE thermal energy (Options 1,2,4,5)
- Electricity cost (all Options)
- Fuel cost (all Options)

The system heat output was found to have little influence on the ultimate VPE steam or thermal energy product cost at base case values and above.

The electrical energy requirements for the thermal energy recovery options could be significantly reduced by recovering pressure energy from the non-condensible VPE gases through the use of an expansion turbine. This possibility, which could reduce system electrical load by 50% or more, was not considered in the present economic model.

The values of other sensitivity variables are likely more site specific. For example, the value of solid fuel may be zero for some operations, with only a nominal handling cost to be incurred. High pressure, relatively pure carbon dioxide, for "slug" injection in-situ processes may have greater value in more remote locations. In any event, as will be discussed in Section 8, it is imperative that close communication be maintained between oil sand recovery operations, and developers of wet oxidation systems.

In conclusion, the following table summarizes the approximate range of costs which could be anticipated for the six different options. Two ranges are presented for Option 6, one with a carbon dioxide credit, and one without.

	Cost ($/GJ - VPE steam or thermal energy)	
Option	Lowest	Highest
1	4.9	7.2
2	4.9	7.2
3	4.2	6.0
4	6.0	10.0
5	6.0	10.0
6	4.5	6.5
6 (with CO_2 credit)	1.5	4.0

For comparison, CH_2M Hill (1982)(1) reported steam generation costs from a once through steam generator to be $5.40 and $7.95/GJ for a natural gas and crude fired system respectively.

TABLE 7.1 - Option 1 Base Case Cost Summary

Temperature (°C)	Pressure (MPa)	Vapour/Feed (-)	Fuel Concentration (%)	VPE Steam Cost ($/GJ)
310	17.2	0.9	10.0	6.14
300	15.9	0.9	11.4	6.35*
310	17.2	0.8	8.9	6.37
310	17.2	0.8	7.8	6.52
300	15.9	0.8	10.2	6.60

* Actual/Practical Coil Length = 1.06

TABLE 7.2 - Option 1. Sensitivity Variable Summary

Sensitivity Variable	Value		Temp. (°C)	Press. (MPa)	VPE/Feed (-)	VPE Steam Cost ($/GJ)	
	Base Case	New				New	Change from Base Case
Fuel Cost ($/tonne)	41.2	5.	310	17.2	0.9	4.54	- 1.6
	41.2	60.	310	17.2	0.9	6.98	+ 0.84
Elec. Cost ($/Kwhr)	0.03	0.01	310	17.2	0.9	4.58	- 1.56
	0.03	0.05	310	17.2	0.9	7.71	+ 1.57
Heat Output (MJ/Hr)	264,000	100,000	310	17.2	0.9	6.99	+ 0.85
	264,000	350,000	310	17.2	0.9	5.98	- 0.16
Freq. Factor (min^{-1})	452,160	$2.025\text{x}10^6$	310	17.2	0.9	6.12	- 0.02
Activation Energy (cal/mole)	17,927	18,913	310	17.2	0.9		
High Temperature Water Credit ($/GJ)	3.5	2.0	310	17.2	0.9	6.62	+ 0.48
	3.5	5.5	260	14.8	0.9	4.09	- 2.05
Material (Titanium)	Gr. 12	Gr. 7	310	17.2	0.9	6.17	+ 0.03

TABLE 7.3 - Option 2 Base Case Cost Summary

Temperature (°C)	Pressure (MPa)	Vapour/Feed (-)	Fuel Concentration (%)	VPE Steam Cost ($/GJ)
310	17.2	0.9	10.0	6.14
300	15.9	0.9	11.4	6.35*
310	17.2	0.8	8.9	6.36
310	17.2	0.8	7.8	6.51
300	15.9	0.8	10.2	6.59

*Actual/Practical Coil Length = 1.06

TABLE 7.4 - Option 3 Base Case Cost Summary

Temperature (°C)	Pressure (MPa)	Vapour/Feed (-)	Fuel Concentration (%)	Thermal Energy Cost ($/GJ)	Actual/Practical Coil Length (m/m)
260	12.0	0.9	21.0	5.06	1.5
260	12.7	0.9	23.0	5.08	1.69
260	13.4	0.9	25.0	5.10	1.85
260	14.1	0.9	27.0	5.12	2.0
270	12.8	0.9	29.0	5.12	1.48

TABLE 7.5 - Option 3. Sensitivity Variable Summary

Sensitivity Variable	Value		Temp. (°C)	Press. (MPa)	VPE/Feed (-)	Thermal Energy Cost ($/GJ)	
	Base Case	New				New	Change from Base Case
Fuel Cost ($/tonne)	41.2	5.	260	12.0	0.9	3.84	- 1.22
	41.2	60	260	12.0	0.9	5.69	+ 0.63
Elec. Cost ($/Kwhr)	0.03	0.01	260	12.0	0.9	3.96	- 1.10
	0.03	0.05	260	12.0	0.9	6.15	+ 1.09
Heat Output (MJ/Hr)	264,000	100,000	260	12.0	0.9	5.71	+ 0.11
	264,000	350,000	260	12.7	0.9	4.96	- 0.10

TABLE 7.6 - Option 4 Base Case Cost Summary

Temperature (°C)	Pressure (MPa)	Vapour/Feed (-)	Fuel Concentration (%)	VPE Steam Cost ($/GJ)	Actual/Practical Coil Length (m/m)
320	14.8	0.9	17.9	8.54	3.36
320	14.8	0.8	16.0	8.80	1.20
320	14.8	0.7	14.0	8.80	1.20
320	14.8	0.6	12.0	9.17	1.36
320	14.8	0.5	10.0	9.41	< 1.0

TABLE 7.7 - Option 4. Sensitivity Variable Summary

Sensitivity Variable	Value		Temp. (°C)	Press. (MPa)	VPE/Feed (-)	VPE Steam Cost ($/GJ)	
	Base Case	New				New	Change from Base Case
Fuel Cost ($/tonne)	41.2	5.	320	14.8	0.9	5.66	- 2.88
	41.2	60	320	14.8	0.9	10.04	+ 1.50
Elec. Cost ($/Kwhr)	0.03	0.01	320	14.8	0.9	5.62	- 2.92
	0.03	0.05	320	14.8	0.9	11.47	+ 2.93
Heat Output (MJ/Hr)	264,000	100,000	320	14.8	0.9	10.69	+ 2.15
	264,000	350,000	320	14.8	0.9	8.12	- 0.42
Freq. Factor (min^{-1})	452,160	2.025×10^6	320	14.8	0.9	8.52	- 0.02
Activation Energy (cal/mole)	17,927	18,913	320	14.8	0.9		
Material (Titanium)	Gr. 12	Gr. 7	320	14.8	0.9	8.58	+ 0.04
High Temp. Water Credit ($/GJ)	3.5	2.0	320	14.8	0.9	10.6	+ 2.06
	3.5	5.5	320	16.6	0.9	5.77	- 2.77

TABLE 7.8 - Option 5 Base Case Cost Summary

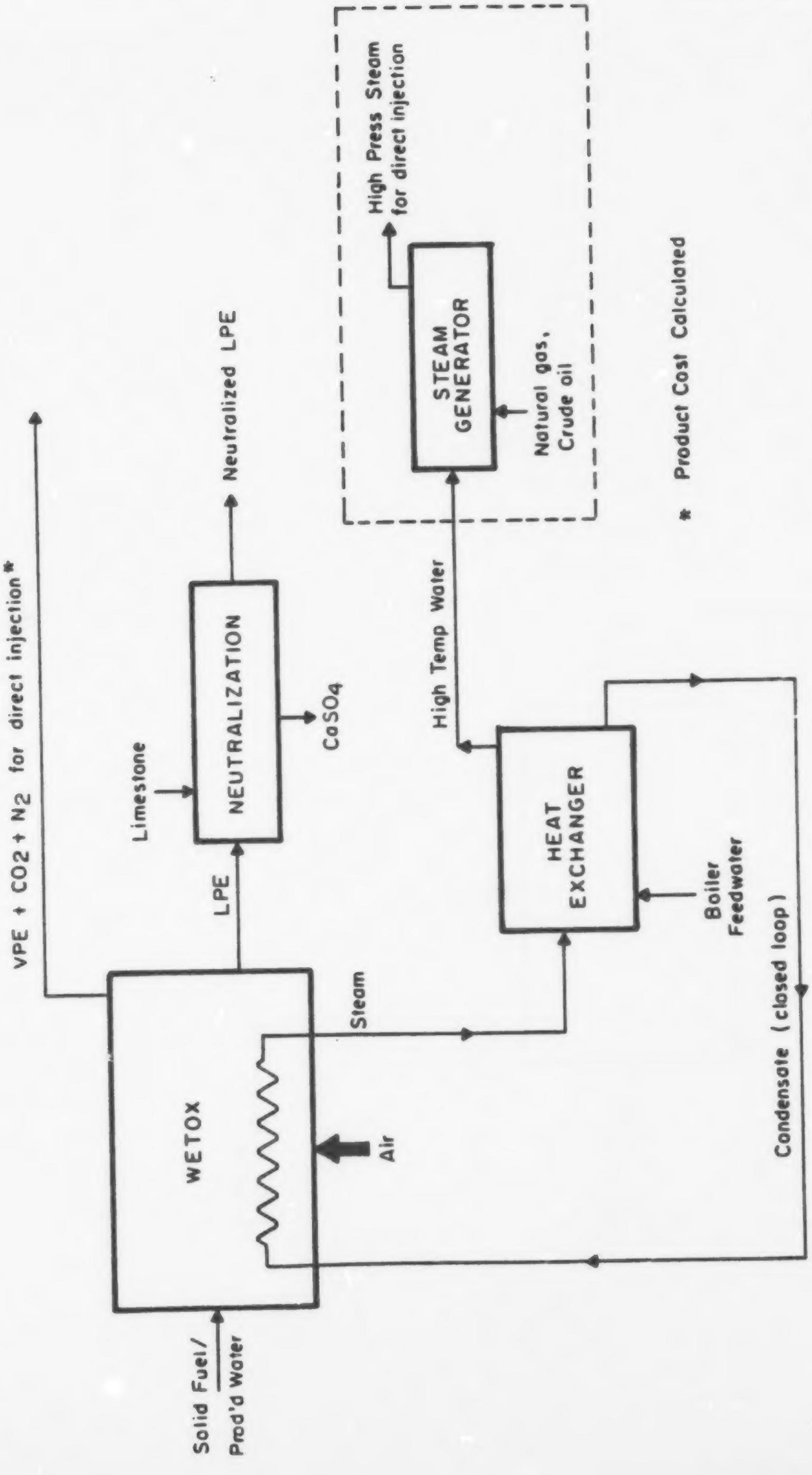
Temperature (°C)	Pressure (MPa)	Vapour/Feed (-)	Fuel Concentration (%)	VPE Steam Cost ($/GJ)	Actual/Practical Coil Length (m/m)
320	14.8	0.9	17.9	8.54	3.36
320	14.8	0.8	16.0	8.66	1.86
320	14.8	0.7	14.0	8.79	1.20
320	14.8	0.6	12.0	9.16	1.36
320	14.8	0.5	10.0	9.39	< 1.0

TABLE 7.9 - Option 6 Base Case Cost Summary

Temperature (°C)	Pressure (MPa)	Vapour/Feed (-)	Fuel Concentration (%)	Thermal Energy Cost ($/GJ)	Actual/Practical Coil Length (m/m)
260	6.4	0.9	21.0	2.79	1.52
270	7.2	0.9	17.9	2.80	1.49
290	10.9	0.9	27.2	2.81	3.48
280	9.9	0.8	28.1	2.82	1.96
280	8.1	0.9	15.3	2.84	1.41

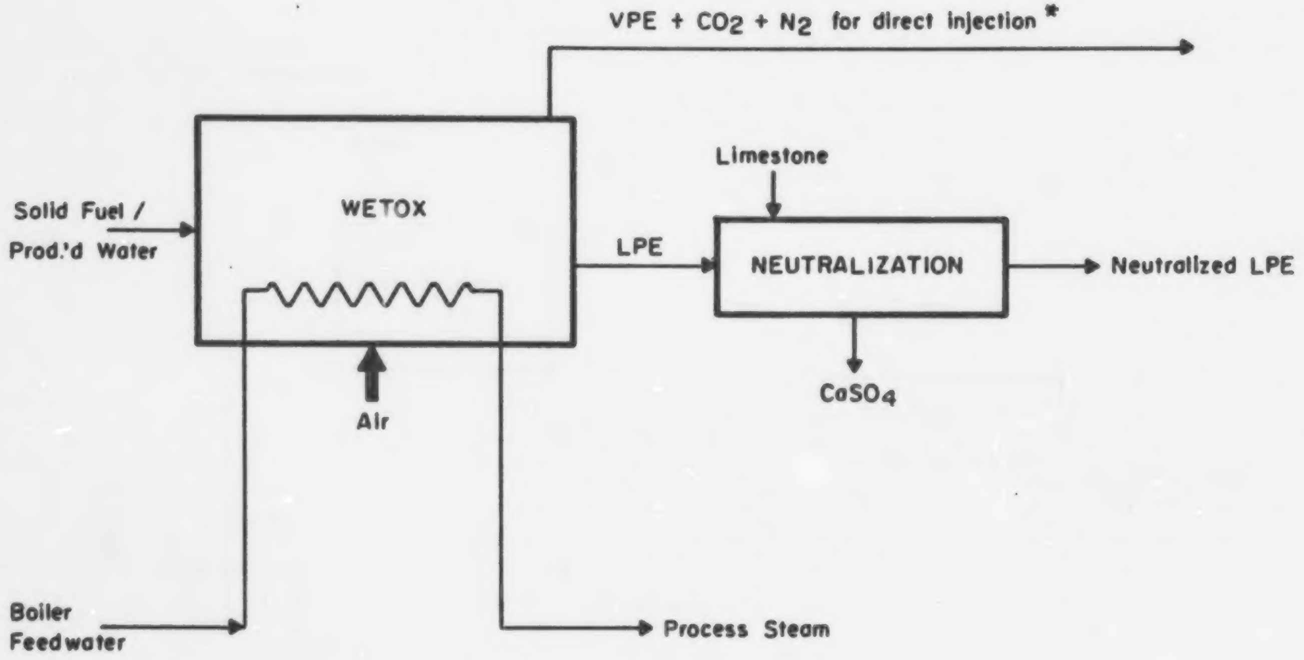
TABLE 7.10 - Option 6. Sensitivity Variable Summary

Sensitivity Variable	Value		Temp. (°C)	Press. (MPa)	VPE/Feed (-)	Thermal Energy Cost ($/GJ)	
	Base Case	New				New	Change from Base Case
Fuel Cost ($/tonne)	41.2	5.	260	6.4	0.9	1.58	- 1.21
	41.2	60.	260	6.4	0.9	3.42	+ 0.63
Elec. Cost ($/Kwhr)	0.03	0.01	260	6.4	0.9	1.59	- 1.20
	0.03	0.05	260	6.4	0.9	4.00	+ 1.21
Heat Output (MJ/Hr)	264,000	100,000	260	7.2	0.9	3.73	+ 0.94
	264,000	350,000	270	7.2	0.9	2.62	- 0.17
Carbon Dioxide Credit ($/kg)	0.03	0	260	6.4	0.9	5.48	+ 2.69
	0.03	0.05	260	6.4	0.9	1.00	- 1.79


Solid Fuel/
Prod'd Water
WETOX
Air
Steam
Condensate (closed loop)
VPE + CO2 + N2 for direct injection*
LPE
Limestone
NEUTRALIZATION
CaSO4
Neutralized LPE
HEAT
EXCHANGER
Boiler
Feedwater
High Temp Water
STEAM
GENERATOR
Natural gas,
Crude oil
High Press Steam
for direct injection

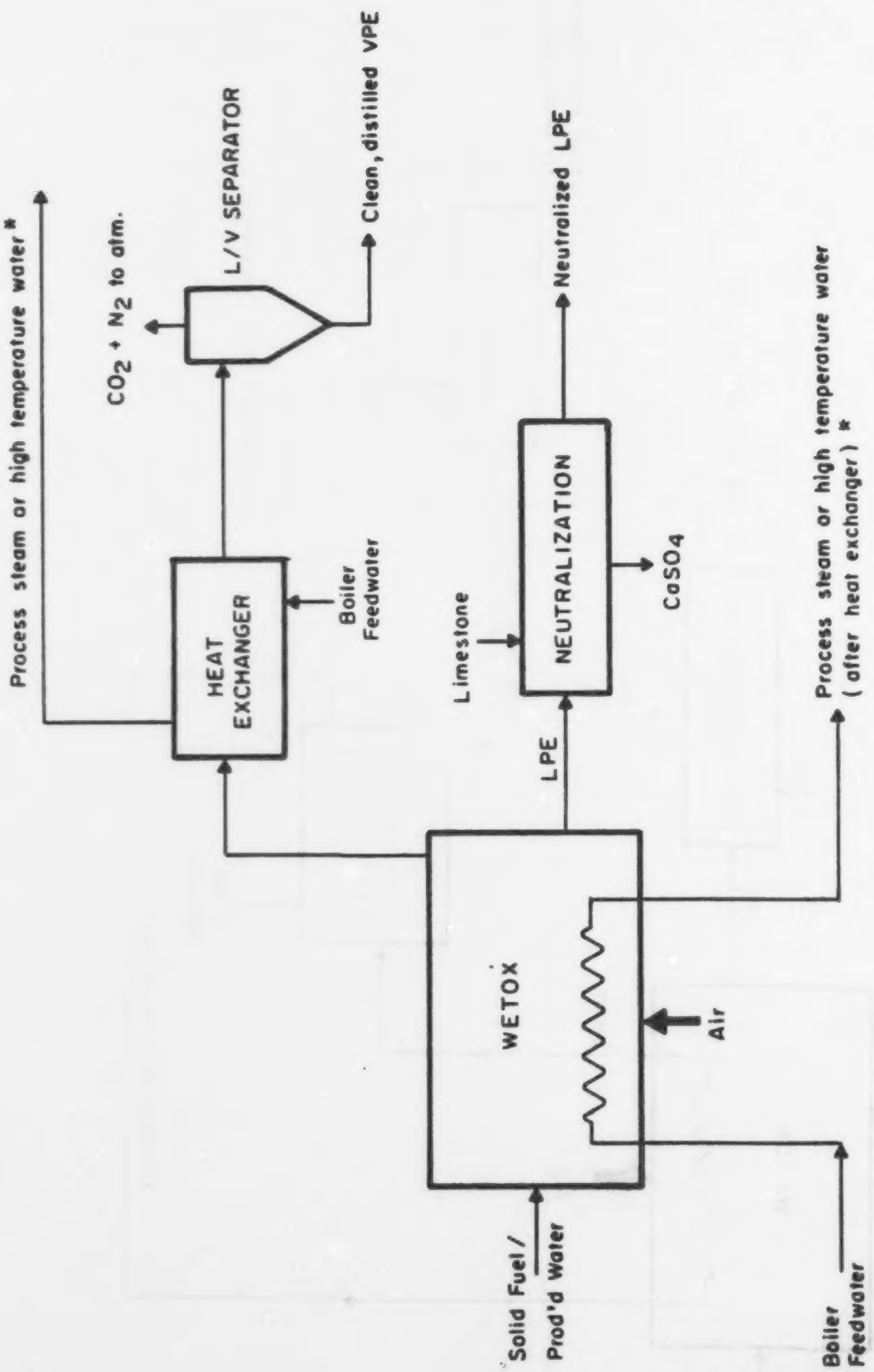
* Product Cost Calculated

FIGURE 7.1 OPTION No. 1.


Solid Fuel /
Prod.'d Water
WETOX
Air
Boiler
Feedwater
Process Steam
VPE + CO_2 + N_2 for direct injection *
LPE
Limestone
NEUTRALIZATION
$CaSO_4$
Neutralized LPE

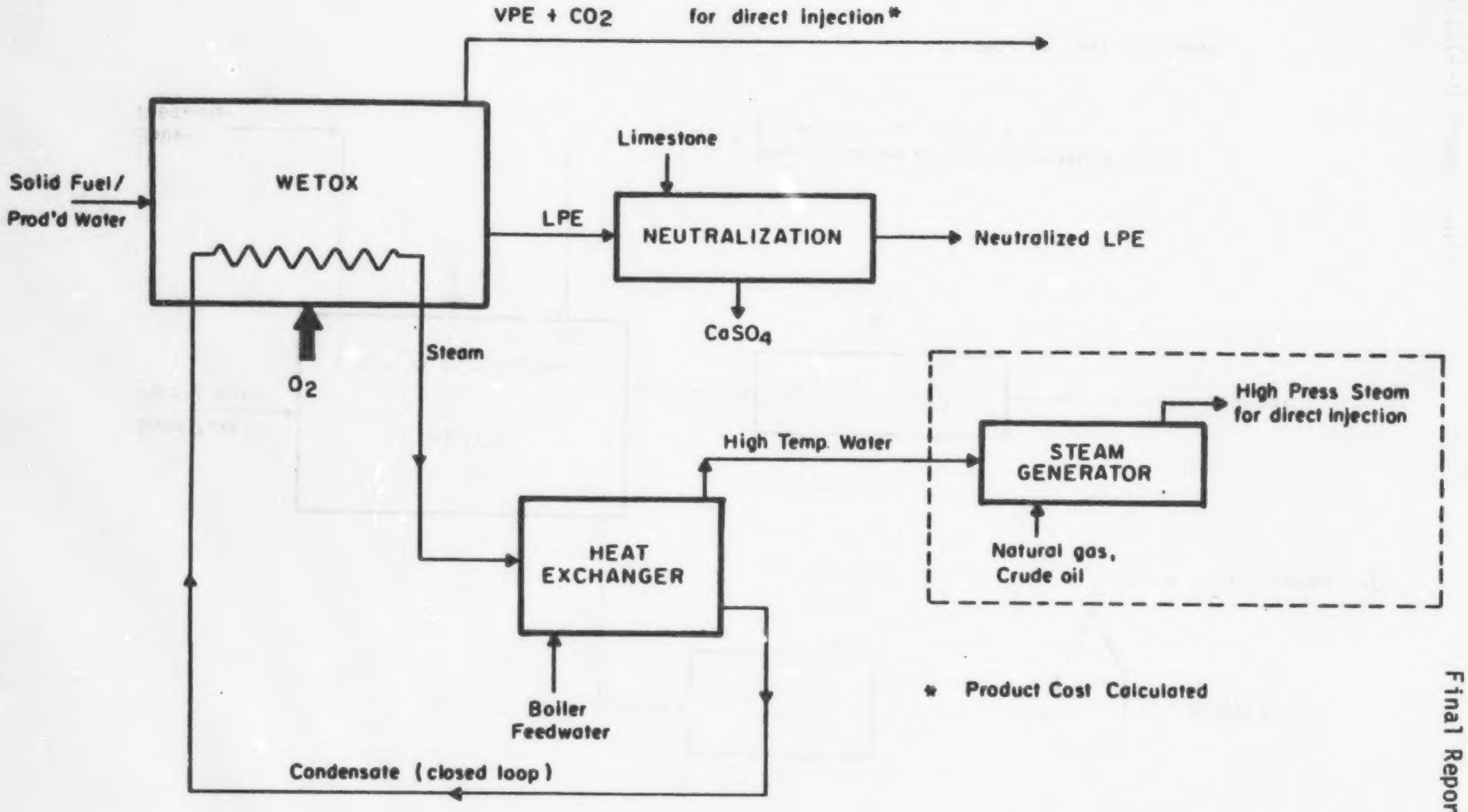
* Product Cost Calculated

FIGURE 7.2 OPTION No. 2.


Solid Fuel / Prod'd Water
WETOX
Air
Boiler Feedwater
Process steam or high temperature water (after heat exchanger) *
LPE
Limestone
NEUTRALIZATION
CaSO$_4$
Neutralized LPE
HEAT EXCHANGER
Boiler Feedwater
Process steam or high temperature water *
L/V SEPARATOR
CO$_2$ + N$_2$ to atm.
Clean, distilled VPE

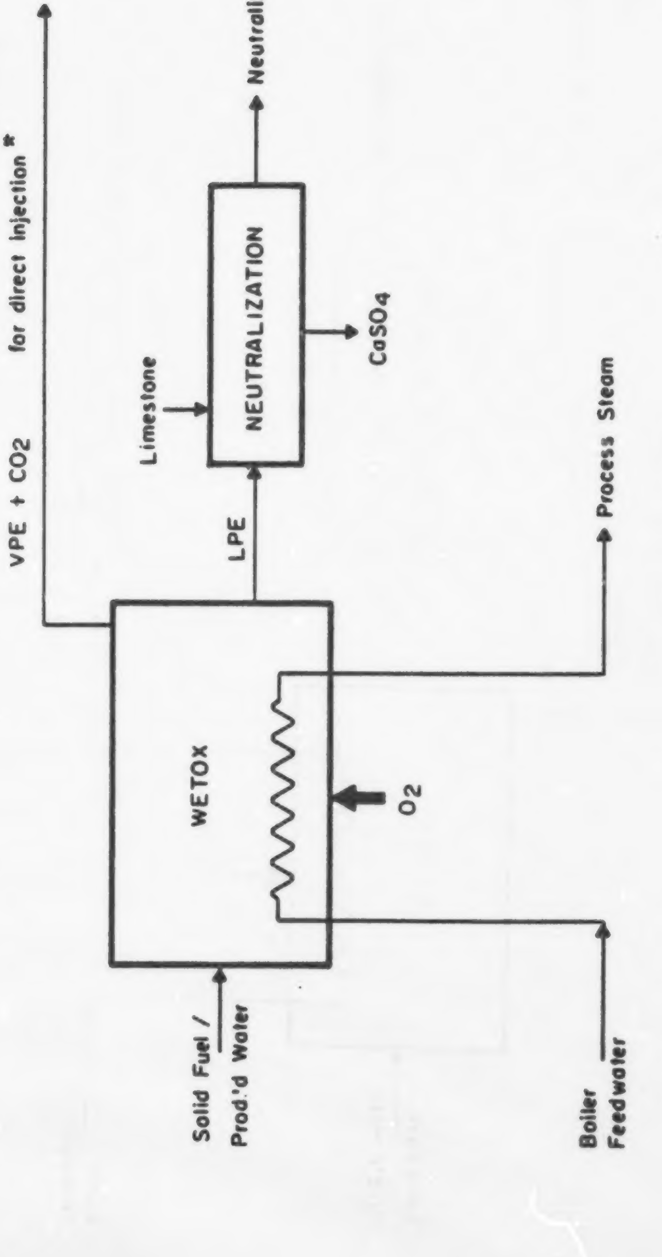
* Product Cost Calculated

FIGURE 7.3 OPTION No. 3


VPE + CO2
for direct injection*
Solid Fuel/
Prod'd Water
WETOX
O2
Steam
LPE
Limestone
NEUTRALIZATION
Neutralized LPE
CaSO4
High Temp. Water
STEAM
GENERATOR
High Press Steam
for direct injection
Natural gas,
Crude oil
HEAT
EXCHANGER
Boiler
Feedwater
Condensate (closed loop)

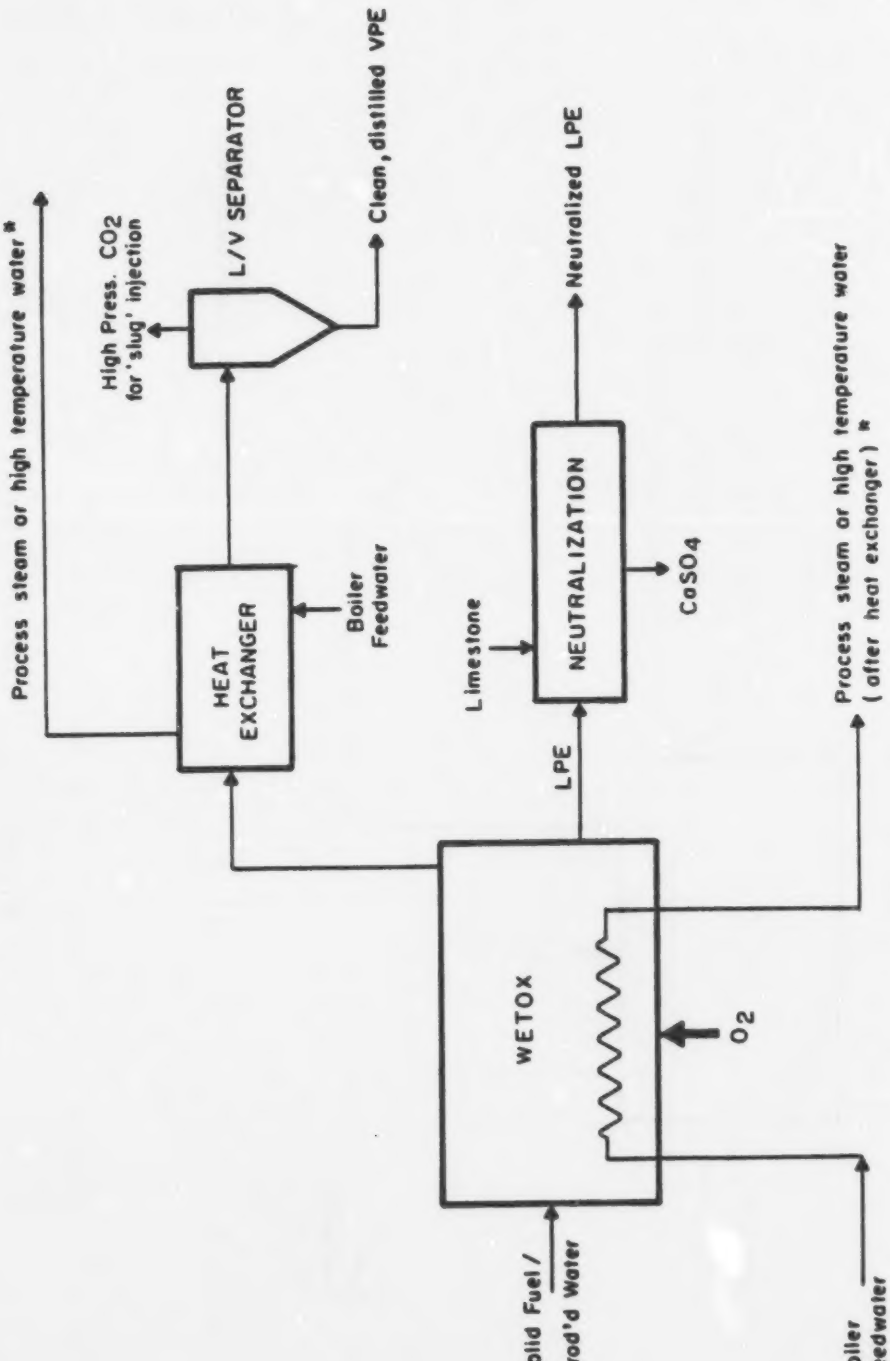
* Product Cost Calculated

FIGURE 7.4 OPTION No. 4


Solid Fuel /
Prod.'d Water
Boiler
Feedwater
WETOX
O_2
Process Steam
LPE
VPE + CO_2
for direct injection *
Limestone
NEUTRALIZATION
$CaSO_4$
Neutralized LPE

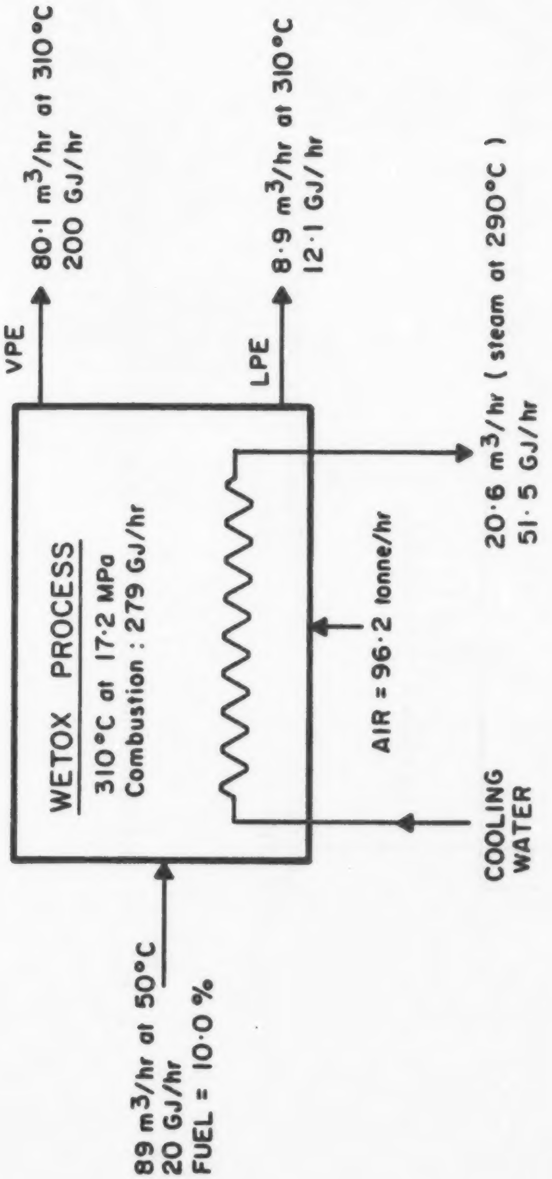
* Product Cost Calculated

FIGURE 7.5 OPTION No.5


Process steam or high temperature water *
HEAT EXCHANGER
Boiler Feedwater
High Press. CO_2 for 'slug' injection
L/V SEPARATOR
Clean, distilled VPE
Limestone
NEUTRALIZATION
$CaSO_4$
LPE
Neutralized LPE
WETOX
O_2
Solid Fuel / Prod'd Water
Boiler Feedwater
Process steam or high temperature water (after heat exchanger) *

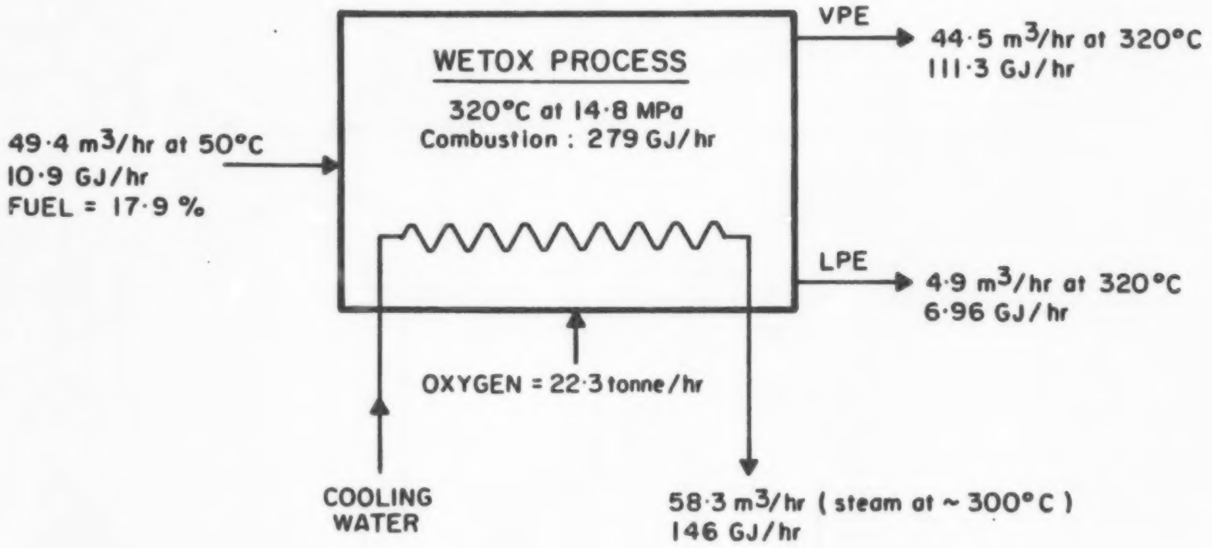
* Product Cost Calculated

FIGURE 7.6 OPTION No. 6


VPE
80·1 m^3/hr at 310°C
200 GJ/hr
LPE
8·9 m^3/hr at 310°C
12·1 GJ/hr
WETOX PROCESS
310°C at 17·2 MPa
Combustion : 279 GJ/hr
AIR = 96·2 tonne/hr
20·6 m^3/hr (steam at 290°C)
51·5 GJ/hr
COOLING WATER
89 m^3/hr at 50°C
20 GJ/hr
FUEL = 10·0 %

* SYSTEM ENERGY AND RECOVERY LOSSES ~ 35·4 GJ/hr

FIGURE 7.7 OPTION No.1 MASS AND ENERGY BALANCES


WETOX PROCESS
320°C at 14·8 MPa
Combustion : 279 GJ/hr
49·4 m³/hr at 50°C
10·9 GJ/hr
FUEL = 17·9 %
VPE
44·5 m³/hr at 320°C
111·3 GJ/hr
LPE
4·9 m³/hr at 320°C
6·96 GJ/hr
OXYGEN = 22·3 tonne/hr
COOLING WATER
58·3 m³/hr (steam at ~ 300°C)
146 GJ/hr

* SYSTEM ENERGY AND RECOVERY LOSSES ~ 25·6 GJ/hr

FIGURE 7.8 OPTION No. 4. MASS AND ENERGY BALANCES

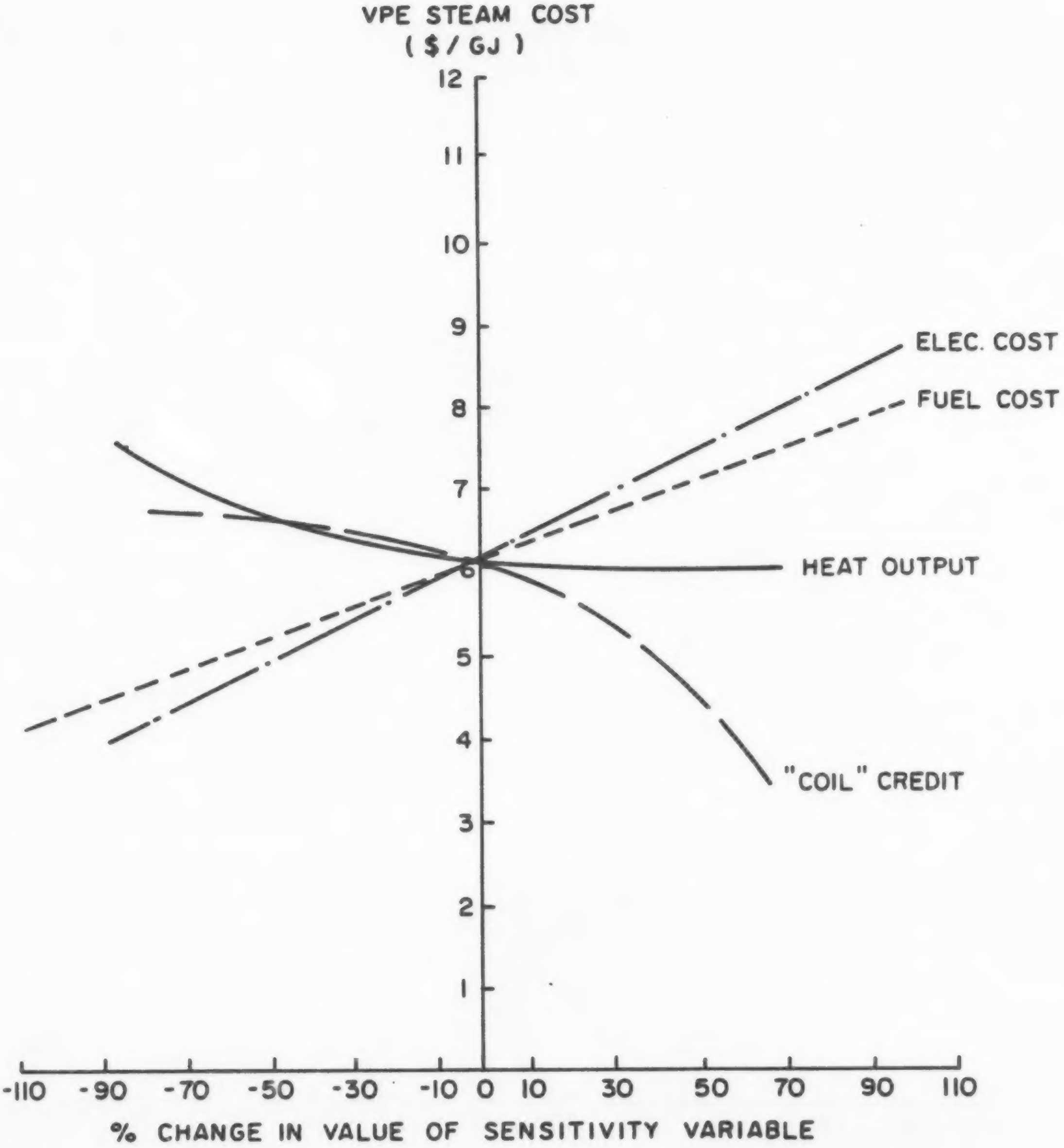


FIGURE 7.9 OPTION No.1. SENSITIVITY ANALYSIS

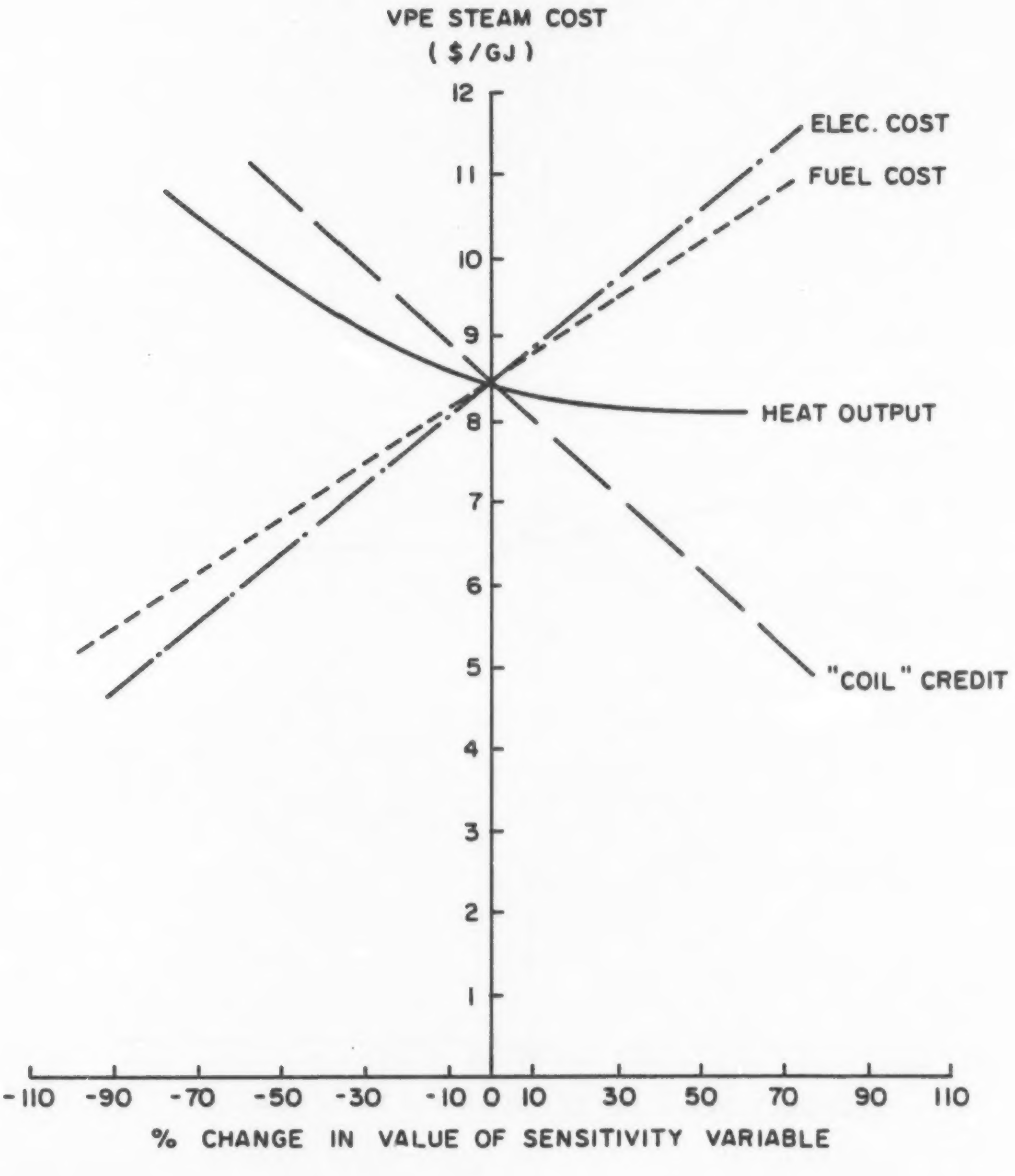
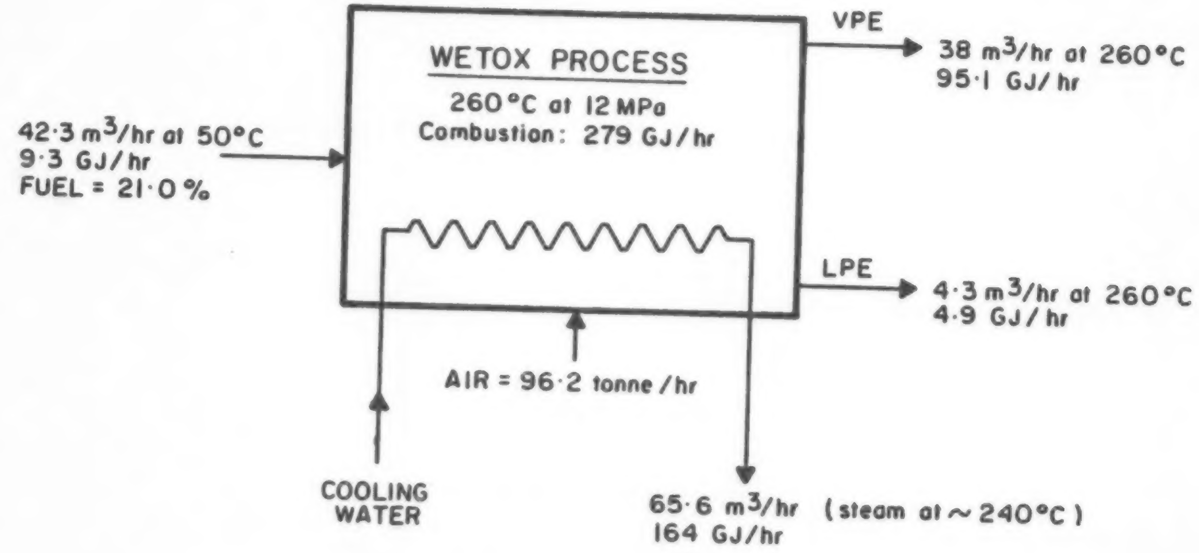
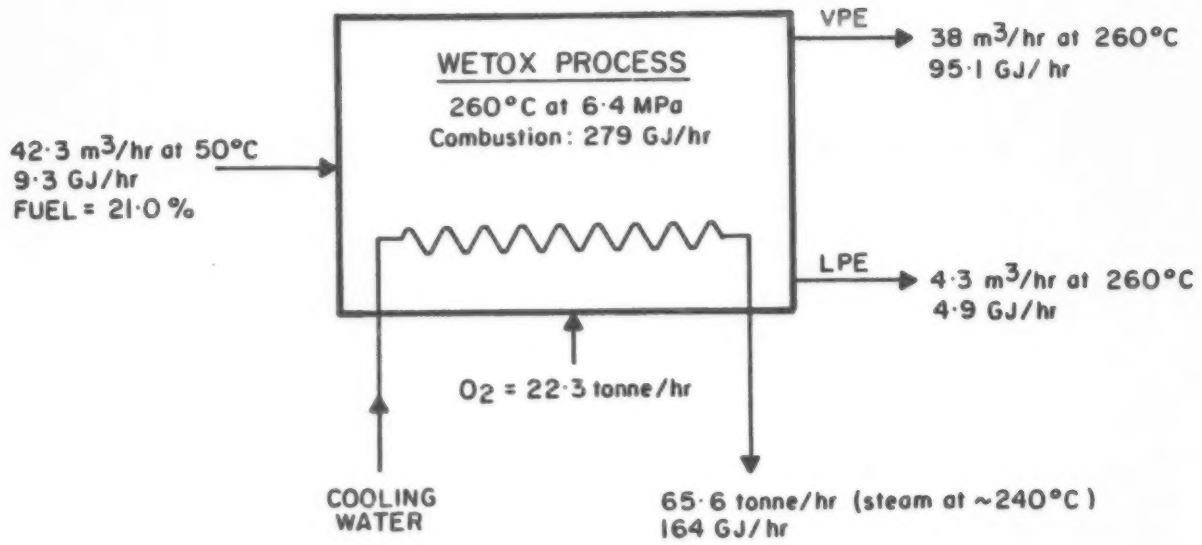


FIGURE 7.10 OPTION No. 4 SENSITIVITY ANALYSIS


WETOX PROCESS
260°C at 12 MPa
Combustion: 279 GJ/hr
42·3 m3/hr at 50°C
9·3 GJ/hr
FUEL = 21·0 %
VPE
38 m3/hr at 260°C
95·1 GJ/hr
LPE
4·3 m3/hr at 260°C
4·9 GJ/hr
AIR = 96·2 tonne/hr
COOLING WATER
65·6 m3/hr (steam at ~ 240°C)
164 GJ/hr

* SYSTEM ENERGY AND RECOVERY LOSSES ~ 24·3 GJ/hr

FIGURE 7.11 OPTION No. 3 MASS AND ENERGY BALANCES


WETOX PROCESS
260°C at 6·4 MPa
Combustion: 279 GJ/hr
42·3 m3/hr at 50°C
9·3 GJ/hr
FUEL = 21·0 %
VPE
38 m3/hr at 260°C
95·1 GJ/hr
LPE
4·3 m3/hr at 260°C
4·9 GJ/hr
O2 = 22·3 tonne/hr
COOLING WATER
65·6 tonne/hr (steam at ~240°C)
164 GJ/hr

* SYSTEM ENERGY AND RECOVERY LOSSES ~24·3 GJ/hr

FIGURE 7·12 OPTION No. 6 MASS AND ENERGY BALANCES

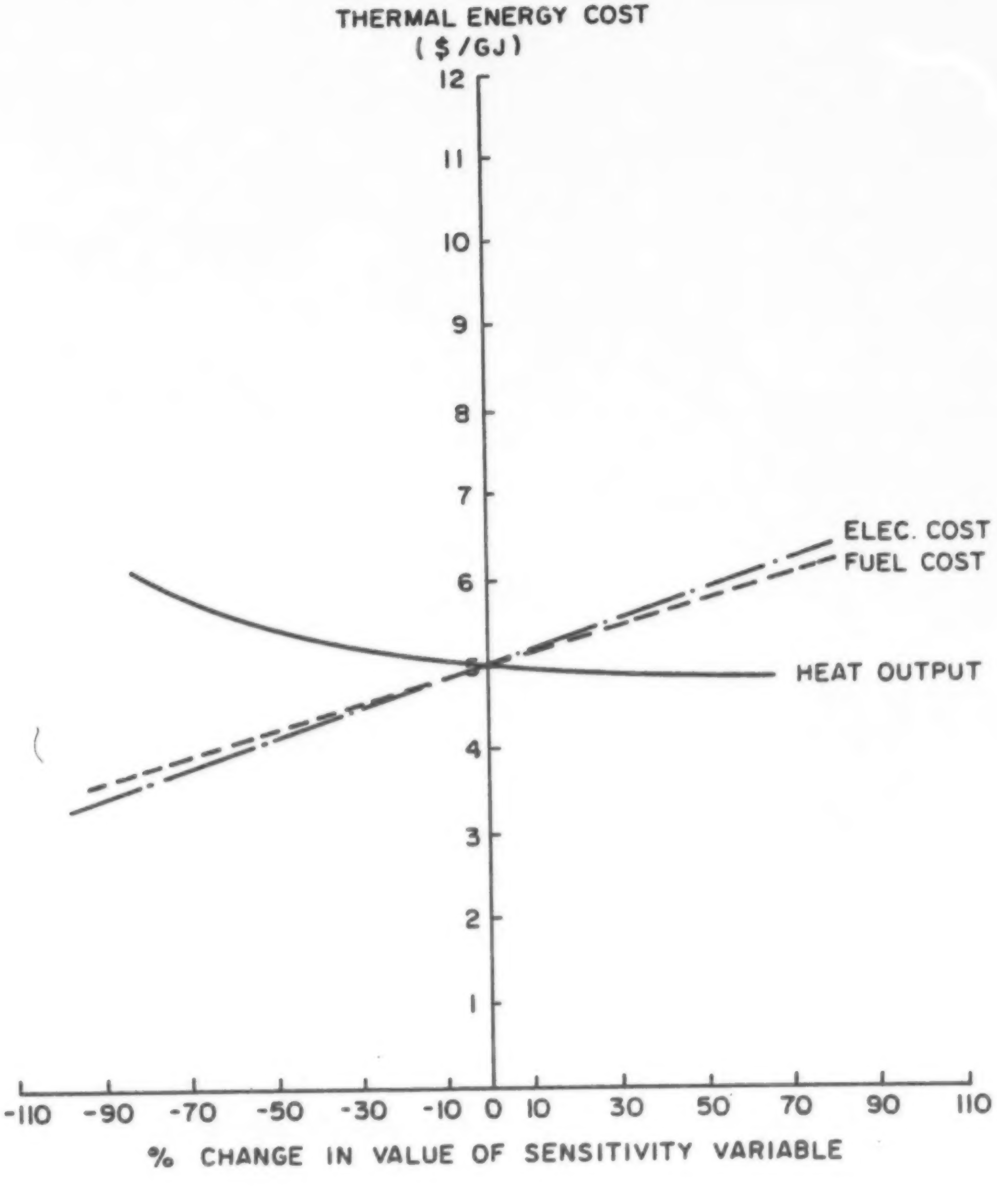


FIGURE 7.13 OPTION No. 3 SENSITIVITY ANALYSIS

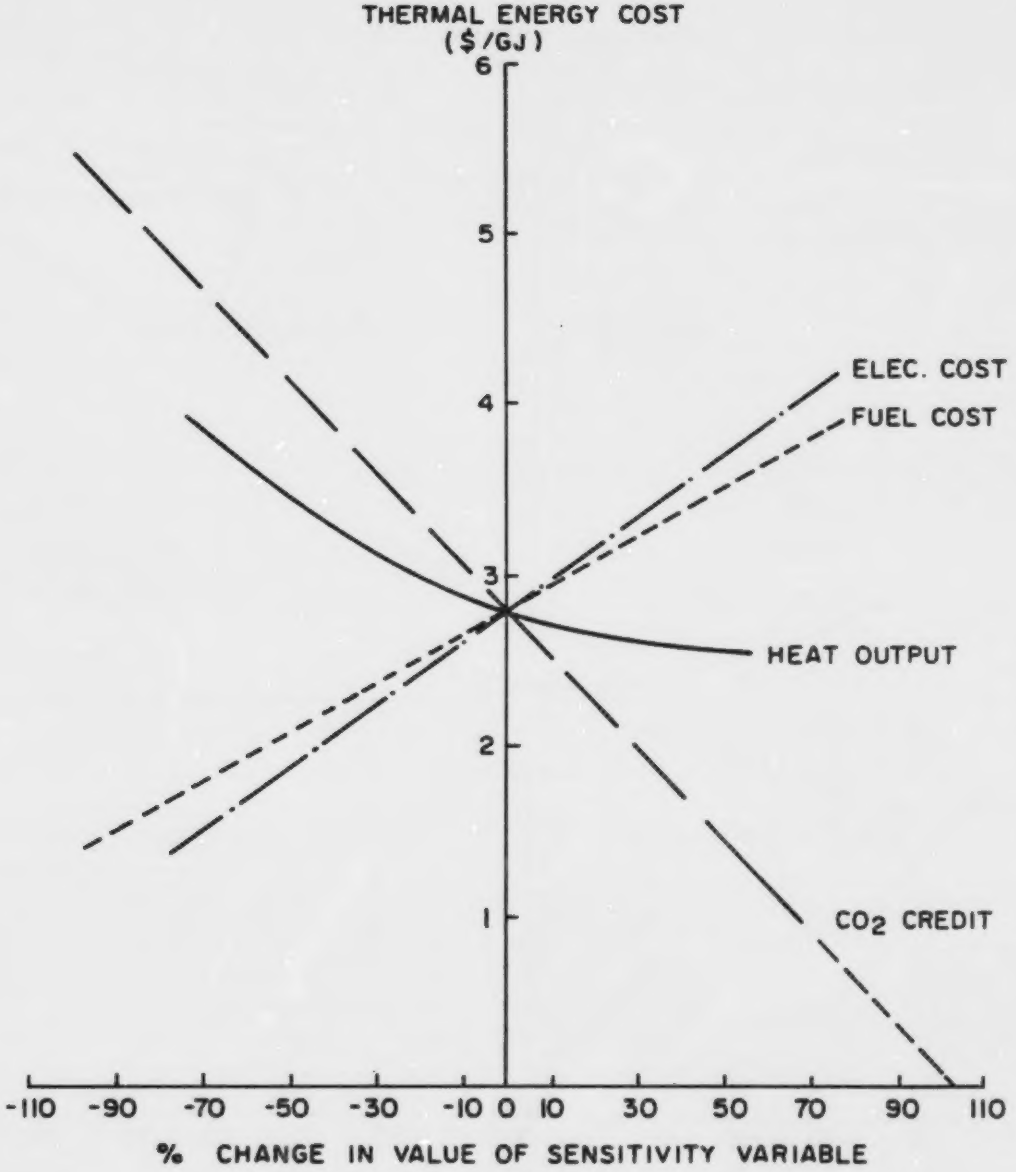


FIGURE 7.14 OPTION No. 6 SENSITIVITY ANALYSIS

8. DISCUSSION AND IMPLICATIONS OF RESEARCH PROGRAM

The results of the research undertaken, and the subsequent technical and economic assessment, indicate that there is considerable potential for the application of wet oxidation in oil sand recovery operations. Unfortunately, however, all of the kinetic data were developed on small batch units, without confirmation on a suitable pilot plant scale. Existing Wetox pilot plant equipment is not designed for the rather severe operating conditions required for solid fuel/produced water treatment.

The free bitumen contained in produced water should be minimized. Directing raw produced fluids from the wellhead to a wet oxidation system is not considered to be a viable alternative. There are a number of reasons for this:

- Feed lines, pumps, etc., would be severely affected by fouling, particularly for equipment operating at elevated temperatures.

- The reaction characteristics are not as favourable as for the solid fuels. The net effect is a reduction in system efficiency, plus an increased liquid post treatment requirement.

- Thermal cracking, resulting in volatilization of lighter constituents would almost certainly occur. Again, system efficiency would suffer, and vapour phase treatment requirements would increase.

The solid fuels tested in the program are particularly well suited to wet oxidative treatment. An abnormally prolonged initial rapid reaction regime is apparent, which proceeds until essentially 90 to 95% destruction is realized. This characteristic effectively reduces required reactor residence time, and dramatically reduces post liquid phase treatment requirements.

As discussed in detail in the sections pertaining to fluid & delayed coke treatment, there is considerable uncertainty as to the actual effect of pH on the combustion reaction kinetics. In an operating system high solid fuel concentrations plus high evaporation rates, will result in significant concentrations of sulfuric acid. It is desirable to at least partially neutralize the acids concurrent with their production. If sodium hydroxide or limestone can be fed into the vessel with the solid fuel/produced water slurry without a significant drop in reaction rate, then potential corrosion problems would be reduced.

The maximum rate of evaporation during reaction is another uncertainty which can only be confirmed through continuous flow pilot plant testing. Advantages of increased evaporation will include:

- liquid retention time is greater which effectively reduces reactor size for a given flowsheet.

- the VPE is free of dissolved solids and its post treatment requirements would be significantly less than for the LPE.

- the LPE is concentrated, increasing the potential for recovery of valuable heavy metals solubilized during reaction (e.g. vanadium, titanium, nickel, etc.)

- solid fuel concentrations can be increased with higher evaporation rates, resulting in further reduction in reactor size for a given heat output.

Although increasing the evaporation rate is not expected to affect the solid fuel oxidation reaction, the more complex bitumen (contained in the produced water) reactions may be changed. Increased evaporation will result in an increase in the volatilization of some lighter hydrocarbons and other reaction by-products. The best solution to this problem may be to apply a vapour phase catalytic system on the outlet of the reaction vessel. Preliminary indications during this research program are that this may, indeed, be feasible, but additional research is required.

The patented modification to the Wetox process has increased the number of options available for the application of wet oxidation in oil sand recovery operations. Furthermore, an increase in the energy released per unit reactor volume, and, therefore, a reduction in capital cost for given energy output, is realized. The implications of the patent are significant. The preferred fluid in the cooling coils is water, which would gain latent heat through steam flashing. If high temperature water was the preferred energy product, the working fluid would still be steam (to maximize the system heat removal), with operation in a closed loop, evaporation-condensation configuration.

The choice of low pressure process steam or high temperature water product depends on the demand of the application. In a steam stimulation type in-situ process, for example, high temperature water may be preferred. This water could then be pumped through a once-through steam generator. Since approximately half of the total energy required for high pressure steam could then be available as sensible heat, the steam output of a given generator would be increased effectively by a factor of about two and energy costs (e.g. for natural gas, crude oil) would be correspondingly decreased.

The manner in which the present computer model is constructed will permit the possible future inclusion of the capital and operating costs of a conventional steam generator.

Alternatively, low pressure process steam may be the preferred product in an oil sands mining complex. The steam could be utilized to drive electrical generators, while the turbine outlet steam could support the energy requirements in the hot water extraction process. Operation in the co-generation mode could result in overall energy efficiencies in excess of 70%. The liquid feed to the Wetox process in this case would be tailings rather than produced water. Advantage is also taken of the alkalinity of the tailings, which would reduce potential corrosion problems and costs for post neutralization chemicals.

The decision on whether to employ an air or oxygen based wet oxidation system is difficult, and one that should certainly not be made without reference to the application. If carbon dioxide does, indeed, improve oil recovery rates and efficiency, then an oxygen based system would be preferable and a dollar value should be given for the recovered CO_2. Wet oxidation is particularly attractive for carbon dioxide production because the system is most efficient when operated with low excess oxygen in the off gas.

The quality of the carbon dioxide in the combustion gases and the desired CO_2/steam ratios should be ascertained. If pure carbon dioxide in the combustion gases is not necessary, consideration would be given to enriched air produced simply using a molecular sieve process instead of the more expensive and energy intensive cryogenic type processes. The CO_2/steam ratio for a wet oxidation system using solid fuel is approximately 0.22 kg/kg (calculated on the basis of total Wetox heat output, not just the VPE steam).

A further element in the air versus oxygen debate is the availability of options for the injection of carbon dioxide. If a CO_2 "slug" is deemed most advantageous for oil recovery, then Option 6, which provides for this possibility, should be considered. The credit given for the carbon dioxide was found to have a dramatic impact on the cost of the thermal energy product. For example, if the credit was $0.06/kg ($3.20/Mcf), the net cost of the energy recovered would be essentially zero. Furthermore, the carbon dioxide so collected would already be at high pressure, eliminating (or almost) the need for compression. No credit was given for this fact in the economic analysis.

In summary, the present research has developed the fundamental kinetics of low grade solid fuel and produced water wet oxidative treatment. Pilot plant testing was attempted, but unsuitable equipment design for the application precluded confirming the reaction characteristics. A few practical problems, such as the need for agitation with ground solid fuel, and the fouling problem associated with bitumen treatment were identified. These and other practical problems will be considered in designing pilot scale equipment devoted to demonstrating the efficacy of the application.

9. SOLID FUEL/PRODUCED WATER WETOX PILOT PLANT

9.1 Justification

A major deficiency of this extensive research program was the inability to confirm the batch scale oxidation reaction kinetics on a suitable pilot plant scale. The existing pilot plant at Ontario Research was inadequate for a number of reasons, including:

- The maximum operating pressure is less than that necessary for realizing sufficient oxygen partial pressure for practical solid fuel oxidation reaction rates.
- The maximum operating temperature of the unit is less than that required to realize appreciable reaction rates.
- The heat exchange systems are not designed properly to accept either produced water (with bitumen) or the relatively high specific gravity solid fuels.

On the basis of the Technical and Economic Assessment (Section 7), there appears to be considerable potential for the application of the Wetox process in oil sand recovery operations. Therefore, it is recommended that a pilot scale unit be designed and constructed that would be devoted to solid fuel/produced water treatment. This unit would be constructed incorporating the patented modification to the Wetox process.

Furthermore, the process pilot plant could be used to assess low grade coal wet oxidative treatment for steam generation in Eastern Canadian thermal power plants.

Technical details which must be investigated in this pilot plant will include:

1. Effect of 80% or greater evaporation in the Wetox process (i.e. on the reaction rates, lighter hydrocarbon volatilization, etc.).

2. The feasibility of vapour phase catalytic treatment for removal of residual organics in the Wetox VPE.

3. Effect of pH on solid fuel oxidation reaction kinetics.

4. Liquid phase effluent treatment requirements - potential for mineral recovery (e.g. vanadium, titanium, nickel, etc.).

5. Longer term corrosion testing.

6. Longer term problems associated with mechanical process equipment (e.g. pumps, heat exchanger fouling, let down valves, etc.).

7. Heat transfer efficiency in internal heat recovery coils.

9.2 Pilot Plant Description (Preliminary)

An example of a Wetox pilot plant which may be suitable for solid fuels and/or produced water treatment is described below, and preliminary equipment costs are presented in Section 9.3.

General:

- 12" dia x 48" long (30.5 cm x 122 cm)
- 4 equal sized chambers
- Heat recovery coils installed in each chamber
- Active liquid capacity: 60 L
- Magnetic drive agitators (4)
- Titanium Grade 12 or 7
- Tube in Tube heat exchanger

Operating Data:

- Maximum temperature: 300°C
- Design operating temperature: 280°C
- Pressure: 14 MPa
- Liquid flowrate: approximately 1-4 L/min

• Air flowrate:	approximately 500 L/min
• Solid fuel flowrate:	approximately 0.05 - 0.6 kg/min

Heat Output:

- 0.5 - 1.5 GJ/hr

Pumping System:

- Blowcase or diaphragm

Control Systems:

- Pressure controller C/W control valves, alarms shutdown
- Temperature control (1st chamber of reactor) to control:
  - (i) heaters for start-up
  - (ii) high temperature alarms, shutdown
  - (iii) coil fluid flowrate
- Temperature controls (2nd, 3rd, 4th chambers): C/W control valves for coil fluid flowrates

Pressure Relief Systems:

- Series rupture disc with in line pressure relief valve.
- Rupture disc

9.3 Preliminary Cost Estimate

The cost of major Wetox components were obtained from manufacturers based on the previous pilot plant description. Other components were estimated. The total cost was estimated to be $320,000 and $400,000 for a system fabricated from solid titanium Grade 12 and 7 respectively. A breakdown of the costs of given in the following:

	Cost ($1,000)	
Component	Ti Grade 12	Ti Grade 7
Reactor	30	75
Internal Coils*	10	20
Agitators	35	45
Compressor	86	86
Heat Exchangers/Coolers*	10	20
Heaters*	10	10
Pump*	20	20
Instrumentation*	50	50
Electrical*	10	10
Installation*	30	30
Contingency*	29	34
Total	320.	400.

*Estimated

10. CONCLUSIONS

A concise listing of the conclusions derived during this research program are given in the following. Elaboration of each of these points is given in Section 8, Programme Discussion and Implications.

- Directing raw produced fluids to a wet oxidation system, without primary bitumen removal, should be avoided.
- The Arrhenius relationship for produced water is not linear over the temperature range studied, indicating that the reaction is complex.
- The produced water oxidation reaction can be reasonably well represented by two first order consecutive reactions, typical of most organic materials in wet oxidation. The inflection point between the first and second regimes occurs after 45 to 75% COD destruction has been achieved.
- Copper catalyst is effective at enhancing the rate of reaction for produced water.
- Lower pH values also result in greater reaction rates.
- Steam stripping of lighter organics will likely occur during treatment of produced water. Preliminary indications are that a vapour phase catalytic reaction may reduce the concentration of these contaminants.
- Oxydesulfurization of petroleum coke, while still retaining the carbon relatively intact, is not a feasible treatment alternative. The rate of sulfur oxidation to sulfate is very similar to the carbon oxidation reaction rate.

- The solid fuels tested in this research are particularly attractive candidates for complete oxidation for direct energy recovery from the wet oxidation process. A prolonged first reaction (rapid) is apparent, which proceeds until over 90% of the influent COD has been destroyed.

- Copper catalyst enhances the oxidation reaction rate of solid fuels.

- The rate of the solid fuel oxidation reaction is sensitive to oxygen partial pressures below approximately 1.7 to 2.0 MPa.

- An induction or initiation time is apparent for fluid coke only. Anionic surfactant addition, or a low temperature preheat cycle, eliminates this time, with no apparent effect on the absolute reaction rates.

- Considerable care must be taken in equipment design to minimize problems associated with solid fuel particle precipitation. This includes efficient agitation and high pipe velocities.

- Titanium Grades 2, 7 and 12 were found to be adequate construction materials for this application. Hastelloy C-276, 316 stainless steel or Carpenter 20 alloy are not suitable.

- A patented modification to the wet oxidation reactor arose from the research which allows for substantially higher energy output per unit reactor volume to be realized as compared to the unmodified system. The result is lower system capital costs.

- A computer aided technical and economic assessment indicated a considerable array of options for the application of wet air oxidation in oil sands recovery operations. Because of this, it is essential that future development of the wet air oxidation technology in this area be done with adequate consultation with experts in oil sands processing.

- Process conditions resulting in the lowest cost of high pressure steam (for direct, in-situ injection) were:

  Air based system:

  Temperature = 310°C
  Pressure = 17.2 MPa
  Vapour Phase/Feedrate = 0.9
  Solid Fuel Concentration = 10%

  At these conditions, the steam cost was calculated to be $6.14/GJ. (The solid fuel was Syncrude coke assigned a value of $41.20 per tonne).

- If thermal energy, in the form of high temperature water or process steam, was the desired product, and a credit was given for relatively pure carbon dioxide, the energy cost was determined to be $2.79/GJ. The process conditions were as follows:

  Oxygen based system:

  Temperature = 260°C
  Pressure = 6.4 MPa
  Vapour Phase/Feedrate = 0.9
  Solid Fuel Concentration = 20%

- The most sensitive variables in the economic assessment were, in order:
    - cost of solid fuels
    - carbon dioxide credit value
    - credit value given to low pressure process steam or high temperature water
    - electricity cost

11. RECOMMENDATIONS

Based on the promising technical and economic outlook for wet air oxidation in oil sands, it is recommended that this work be continued in a suitable integrated pilot plant. The following specific actions are recommended:

1. That a decision be made to proceed to pilot plant testing of the various options discussed in the report.

2. That CANMET, perhaps in association with other interested organizations, fund an extension to the project to design, construct and operate a pilot facility. This extension would consist of the following steps:

   - Meet with oil sands plant operators involved in both mining and in-situ extraction processes. Discussions would focus on the elements of the practical integration of the Wetox process into their operation, which would have an influence on the design of the pilot facility.

   - Meet with government and industry representatives concerned in promoting the use of high sulfur Eastern Canadian coal. These discussions would focus on the possibility of using the pilot facility to evaluate coal combustion or desulfurization in the Wetox process.

   - Evaluate alternative wet oxidation process configurations (e.g. Wetox or Zimpro) and complete a detailed design of the pilot scale facility including a detailed cost estimate.

12. REFERENCES

1. CH2M Hill Canada Ltd.
   Generation of Steam Using Low Grade Fuels and Field Produced Water for In-Situ Oil Recovery.
   Final Report to: Energy, Mines & Resources, Canada, August, 1982.

2. Egglestone, A. E., and Wise, T. H.
   Athabasca Oil Sands - Developments in Extraction & Upgrading
   Presented at the 26th Canadian Chemical Engineering Conference, Toronto, Canada, October, 1976.

3. Chilingaran, G. V., and Yen, T. F. (Eds.)
   Bitumens, Asphalts & Tar Sands Developments in Petroleum Science, 7.
   Elsevier Scientific Publishing Company, 1978.

4. Cadotte, A. P.
   Low Grade Fuel Utilization
   Ontario Research Foundation, Internal Quarterly Report, Report No. 40703, 1980.

5. Chemical Engineers Handbook, 5th Ed.
   Edited by Robert H. Perry and Cecil H. Chilton
   McGraw Hill Book Company, 1973.
   pp 4-9, 4-10

6. Ibid, pp 18-79.

7. Levec, J., & Smith, J. M.
   AIChE Journal 22 (1), 159 (1976).

8. Goto, S., and Smith, J. M.
AIChE Journal 21 706 (1975).

9. Ibid, pp 714.

10. U. S. Patent 3,823,088, July, 1974.

11. U. S. Patent 3,948,808, April, 1976.

12. U. S. Patent 3,992,295, November, 1976.

13. U. S. Patent 3,997,440, December, 1976.

14. U. S. Patent 4,062,772, December, 1977.

15. Annual Book of ASTM Standards, 1977, Part 10, Section G.
American Society for Testing & Materials, 1979, Easton, Md., U.S.A.

16. Schutz, Ronald W., and Covington, L. C.
Hydrometallurgical Applications of Titanium
Industrial Applications of Titanium & Zirconium: 3rd Conference
ASTM STP 830
R. T. Webster & G. S. Young, Eds., American Society for Testing & Materials, 1984, pp 29-47.

17. Personal periodic communication (1984) with Arthur Forrest, General Manager, Titanium Company Ltd., Montreal, Canada.

18. Corrosion Tables, Stainless Steels
Distributed by Western Alloys & Metals, Mississauga, Canada
Printed by Caslon Press Offsettryckeri AB, Stockholm, Sweden, 1979.

19. Chemical Marketing Reporter
Schnell Publishing Company Inc., September, 1984.

20. Holland, F. A., and Chapman, F. S.
Liquid Mixing and Processing in Stirred Tanks
Reinhold Publishing Company, New York, N.Y., U.S.A., 1966
pp 134-138.

21. Shreve, R. Norris, and Brink, Joseph A., Jr.
Chemical Process Industries, 4th Ed.
McGraw Hill Book Company, U.S.A., 1977
p 110.

22. Private Communication, February, 1984
Dean Wallace, Oil Sands Sample Bank, Alberta Research Council

APPENDIX A

2 Litre Autoclave

EQUIPMENT

The 2-litre autoclave (Figure 1) has a total capacity of 2 litres with an active liquid volume of about one litre at the temperatures and pressures employed. The reactor is equipped with a variable speed stirrer mounted centrally in the vessel. The maximum operating temperature is 300°C.

The maximum operating pressure is 8.97 MPa.

The schematic for the reactor system is presented in Figure 2.

PROCEDURE

(1) Reactor is loaded with distilled water (minus amount which will be injected to give total of 1 litre)

(2) Reactor is assembled and all necessary connections are made.

(3) Electrical heaters surrounding reactor are turned on.

(4) Injector is loaded and pressurized (injection pressure is usually 300 psi above final reactor pressure).

(5) At desired temperature, injector is opened to expel sample into autoclave.

(6) O_2 is then added as desired and samples taken.

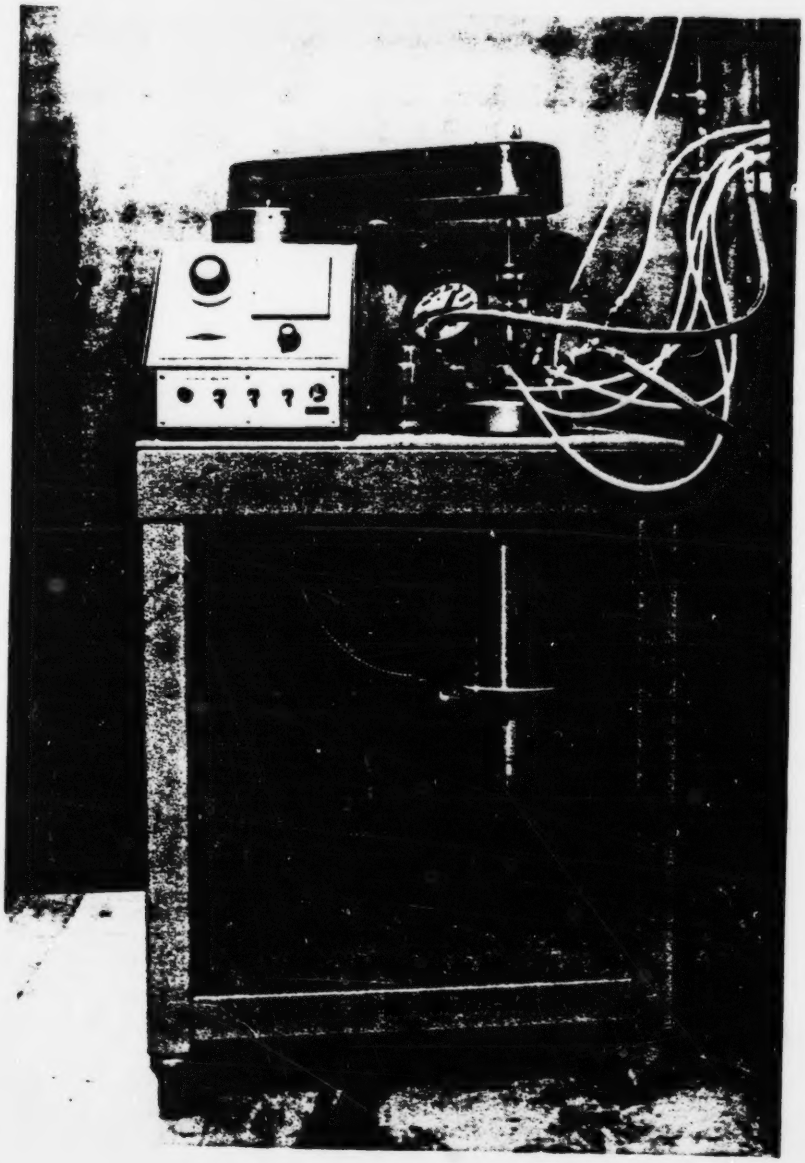


FIGURE 1 - 2-Litre Parr Reactor

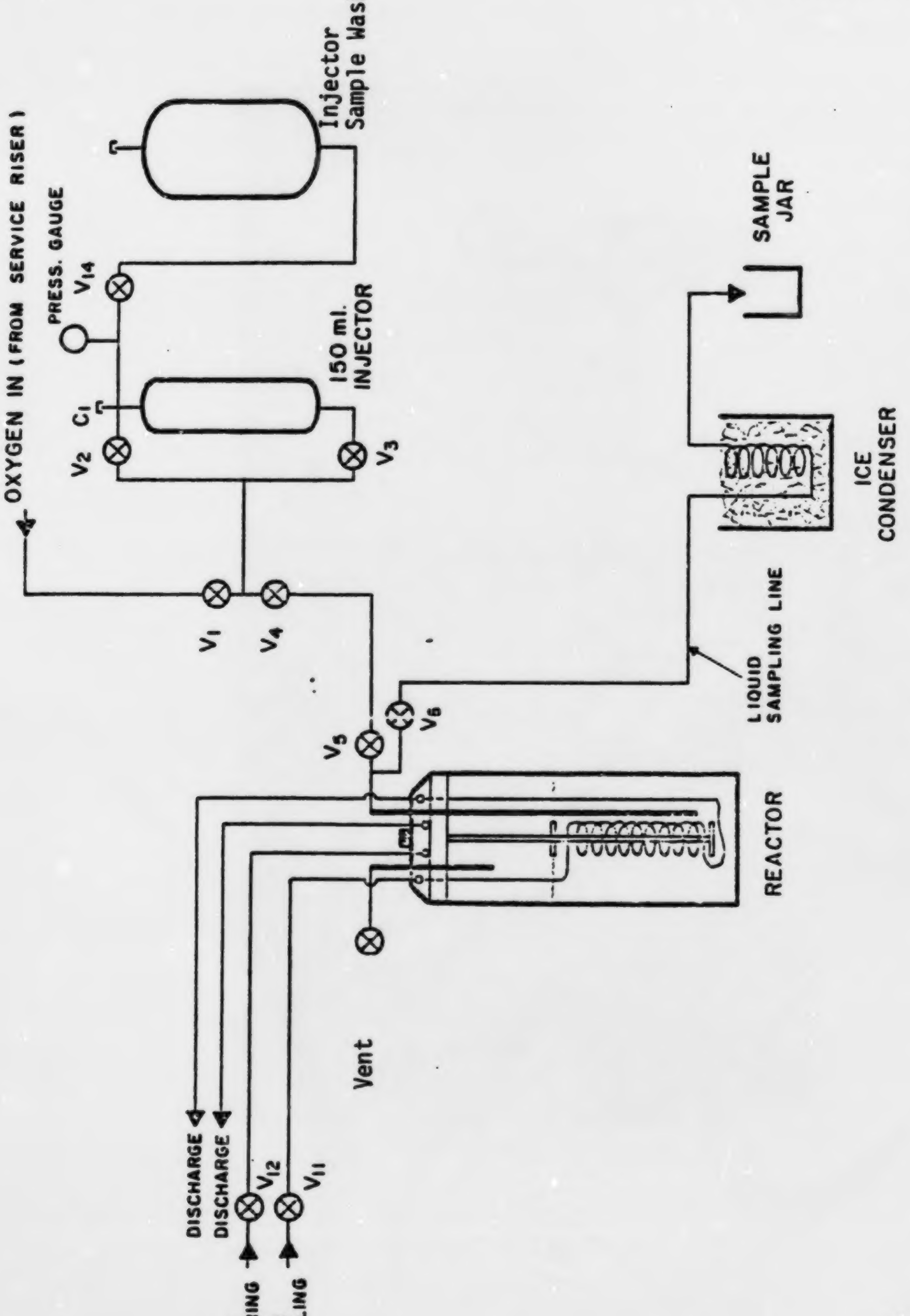

OXYGEN IN (FROM SERVICE RISER)
PRESS. GAUGE
V_{14}
Injector Sample Wash
150 ml. INJECTOR
C_1
V_2
V_3
V_1
V_4
V_5
V_6
SAMPLE JAR
ICE CONDENSER
LIQUID SAMPLING LINE
REACTOR
Vent
DISCHARGE
DISCHARGE
V_{12}
V_{11}
WATER IN FOR STIRRER BEARING
WATER IN FOR REACTOR COOLING COIL.

FIGURE 2 - Schematic for 2-Litre Autoclave

APPENDIX B

1-10 Continuous Flow Unit

EQUIPMENT

The continuous flow Wetox$^{(R)}$ 1-10 unit has a total volume of 10 litres with an active liquid capacity of 5 litres. The inside lining of the reactor and all wetted parts are made of titanium. The process flowsheet is presented in Figure 1.

Agitation

The reactor is equipped with a magnedrive stirrer with a range of 0 → 1500 rpm.

Heating

Two sets of heaters are used to heat the reactants:

1) Electrically heated, Dowtherm heat transfer oil is circulated around the outside of the jacketed vessel.

2) Electrical rod heaters are fixed onto the feed pipe leading to the reactor immediately following the Wetox process heat exchanger. On-off operation of these heaters is controlled via a temperature sensor and relay mounted on the effluent line of the vessel. Because these heaters respond quickly to reactor temperature changes, they are used for pirmary temperature control. At steady state, a system temperature variation of less than ± 5°C is observed.

Reactor Pressure and Air Supply

Compressed air is supplied from a bank of 5 cylinders. The inlet air flowrate is controlled by a micrometer inlet valve. The exit air flowrate, and hence, pressure, is controlled by a Masoneilan Micropak Control Valve.

A rupture disc (1200 psi) is provided on the reactor. Maximum normal operating pressure of the equipment is 700 psi.

Feed System

The feed sample is located in a 40 gallon head tank located beside the pump. The feed tank is equipped with an agitator to ensure homogeneous feeds.

Liquid System

The feed liquid is pumped via a high pressure Moyno progressive cavity type pump through a tube in tube heat exchanger, countercurrently to the process effluent streams. Thereafter, the hot liquid flows through a set of strap-on preheaters prior to entering the reaction vessel.

The liquid level inside the vessel is maintained with a capacitance type probe which, when activated, signals on-off operation of a control valve located after the process heat exchangers.

Vapour System

Compressed air is added continually to the system at the bottom of the vessel below the stirrers. As air is added to the system, its total pressure increases until it exceeds the desired maximum and then a pressure-regulated valve is activated.

All exiting gas is passed through the heat exchanger in which the steam is condensed. The vapour is then further cooled and collected separately.

TEST PROCEDURE

(1) Fresh water is pumped into the reactor until the unit is filled; pump is then stopped.

(2) The reactor heaters are turned on (Not Preheaters).

(3) System is allowed to heat to ∿ 10°C above temperature required.

(4) The desired pressure and flowrate of air is then adjusted.

(5) The pump and preheaters are turned on and adjusted accordingly.

(6) Off-gas is monitored for oxygen concentration.

(7) Feed is pumped for ∿ 2 reactor volumes to achieve steady-state concentrations throughout the process.

(8) Samples of LPE and VPC can then be collected.

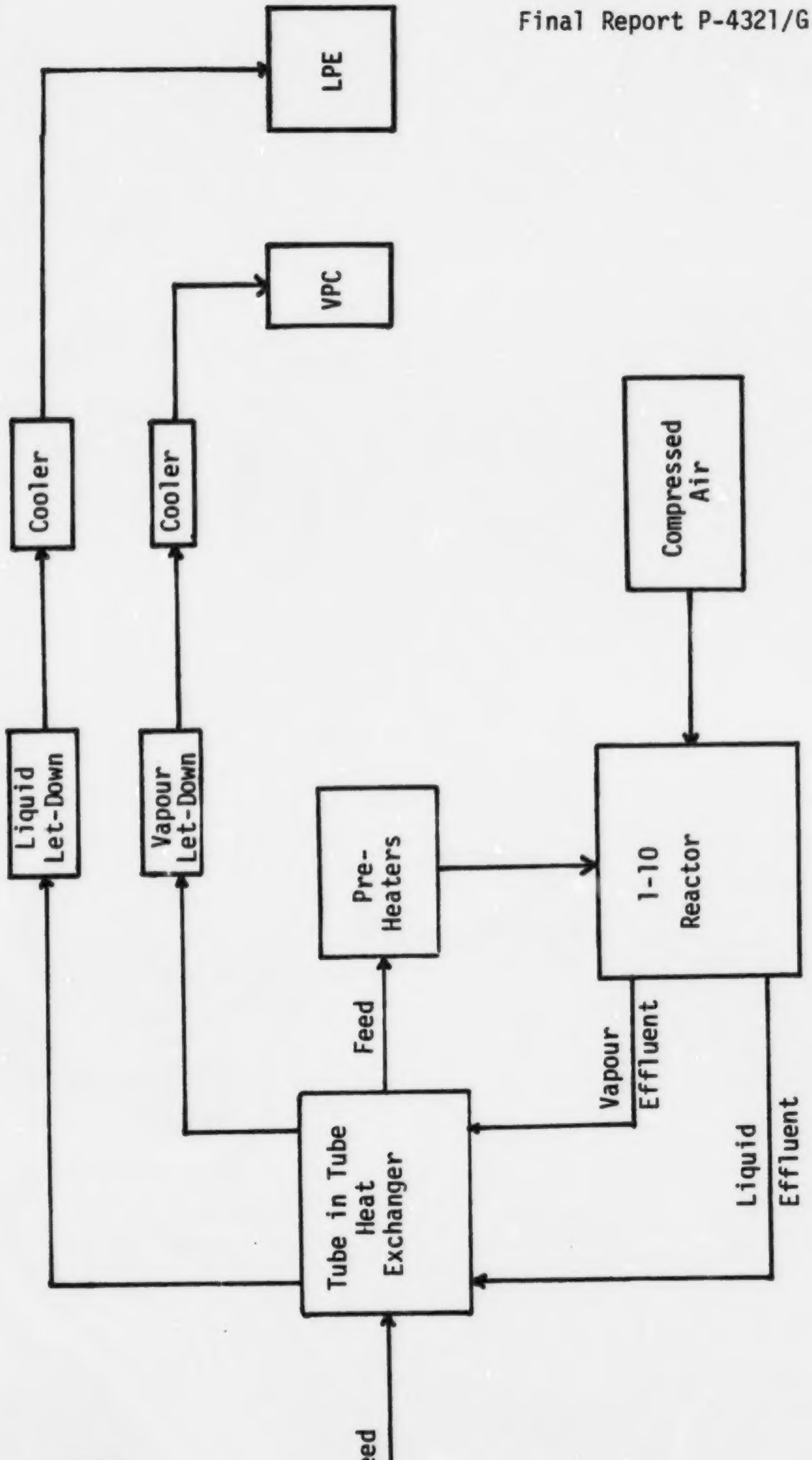

LPE
VPC
Cooler
Cooler
Compressed Air
Liquid Let-Down
Vapour Let-Down
Pre-Heaters
1-10 Reactor
Feed
Vapour Effluent
Liquid Effluent
Tube in Tube Heat Exchanger
Feed
High Pressure Pump

FIGURE 1 - Continuous Flow 1-10 Unit

APPENDIX C

Wetox$^{(R)}$ Continuous Flow Pilot Plant

1. INTRODUCTION

The Wetox$^{(R)}$ 4-10 pilot plant is a continuous flow treatment system which is capable of processing from 200 to 600 Imperial gallons per day. The unit is mounted in a truck for on-site testing and demonstrations (see accompanying photograph). The truck also contains a small laboratory to provide analyses during operation.

A process schematic of the 4-10 pilot plant is provided. The assemblance of equipment includes devices to:

(1) feed (pressurized) reactants (air or oxygen and wastewater) to the reactor,

(2) perform wet oxidation in a continuous flow reactor at elevated temperature and pressure,

(3) sample the reactor during the test (while it is at elevated temperature and pressure),

(4) control and monitor the important operating conditions such as temperature and pressure,

(5) discharge and store (depressurized) liquid-phase effluent,

(6) condense and store steam and volatile matter vented with the spent gases from the reactor,

(7) monitor the oxidant level in the spent gases from the reactor.

2. PREPARATION AND STORAGE OF WASTE

The feed sample is pumped into a 200-litre head tank located outside of the truck. The recirculation pump withdraws fluid from the bottom of the tank and provides a divided, valved discharge to the high-pressure pump and to the head tank surface. The line to the high pressure pump is also equipped with a valved fresh water line for rinsing purposes. Where necessary, the head tank is also equipped with an agitator.

3. FEED SYSTEM

The waste is pumped into the reactor system via a high pressure progressive cavity pump.

Compressed air from the 15 h.p. cooled compressor (max. flow of 27 standard cubic feet per minute) is stored in a 2-foot long by 8 inch diameter cylinder or accumulator. The flow from the compressor is automatically controlled to maintain from 4.83 MPa to 6.9 MPa in the accumulator. The discharge from the accumulator is in three parts:

- high pressure air (4.83 MPa) for agitator pressure
- low pressure (0.69 MPa) instrument air
- high pressure air (4.48 MPa) to the reactor.

The latter flow is monitored via a strain-gage flow-meter and controlled. This total air flow is divided into 3 main flows: to compartment 1, to compartment 2 and to compartments 3 and 4. The flow to compartment 1 and to the combined compartments 3 and 4 is monitored via similar strain-gage flow meters. The line to compartments 3 and 4 is thereafter divided. The flow to each compartment is controlled via suitable needle valves. The air enters each compartment through inlets directly below the impellers.

4. WETOX REACTOR

Prints of the detailed drawings of the 4-10 reactor are provided.

Basically the Wetox reactor is a pressurized version of the continuous stirred tank reactor - the CSTR widely used in chemical engineering. The interior is divided into approximately equally sized compartments, each containing a vertically mounted agitator and separate air inlet. The reactants pass continuously through the series of compartments. The flow of reactants is much slower than the speed of mixing in the constantly stirred chambers or tanks, and incoming fluid immediately blends with the much larger mass of constantly stirred liquid already present in the vessel. As fresh wastewater is added to the first compartment, the level of the agitating liquid rises above the overflow opening in the barrier between the first and second compartments - a portion of the liquid spills over into the second compartment and, in so doing, causes a portion of the liquid in the second compartment to spill into the third and so on throughout the reactor. In this manner, the wastewaters cascade from compartment to compartment during treatment, undergoing intimate mixing continuously. At steady state, the concentrations of the reactants in individual compartments are invariant. The rate of reaction and extent (percentage reduction) depend on the mass flow through the reactor and the operating conditions.

The pilot plant reactor is a 10 inch OD, 48 inch long autoclave. The reactants are mixed sequentially in a series of four mixing chambers. The interior of the reactor is subdivided into 5 chambers, four of which are approximately equal in size and contain agitators. The fifth chamber located at the rear of the reactor is smaller than the others; it contains no agitator and serves as a phase-separation basin. Automatically controlled, separate vents for the vapour and liquid phases are located in the settling basin. The chambers or compartments are formed by four approximately equally spaced, vertically positioned plates of 1/4 inch thick titanium metal. Each plate (partition) is fastened securely to the periphery of the reactor shell to form a water-tight dam. Each partition has a small notch or weir at the liquid level, approximately 7.5 inches above the floor of the reactor. The weir in each partition is 0.25 inches lower than that in the preceding wall, causing liquid to cascade from compartment to compartment as fresh influent enters the first compartment.

Each mixing compartment contains a vertically mounted, motor-driven agitator. All impellers are six-bladed turbines. Two titanium, three inch diameter impellers are mounted on each shaft. In all compartments, one impeller is located within 1 inch of the floor of the reactor and the other barely below the surface of the liquid. Each agitator is equipped with double mechanical balanced seals. The speed of rotation is 900 rpm.

External heat can be supplied to the reactor by four electrically heated rods which are inserted externally into four tubular protrusions extending horizontally into the first compartment. Once the reactor is hot and the blow-case pump is operating, a substantial amount of heat is recovered by the heat exchanger described in a preceding paragraph. The two heaters located near the floor of the reactor well beneath the water level are activated as needed by an automatic controller.

Samples of the liquid phase can be removed from any of the mixing compartments as desired during the test by manually operated sampling tubes.

5. HEAT EXCHANGER

Influent exits from the high-pressure pump and enters the first compartment of the reactor via a tube-in-tube heat exchanger (see attached print of detailed drawing). The tubes comprising the heat exchanger are arranged in a horizontal array and enclosed in a thermally insulated rectangular box. The cold influent first is contacted by the vapours and gases vented from the reactor and then by the liquid-phase effluent. The vapour-liquid exchanger has a path length of 20 feet. The liquid-liquid exchanger path length is 70 feet. The surface area available for heat transfer is about 6 square feet in the combined exchangers. When cold water is pumped through the exchangers and into a 400°F reactor by a high-pressure pump, the influent and effluent approach nearly continuous flow. Under these conditions, the overall coefficient of heat transfer is about 150 Btu/hr-ft^2-°F.

6. VAPOUR-PHASE EFFLUENT

Compressed air or pure oxygen is fed continually to each compartment in proportion to the input COD. The incoming gas is introduced through small openings in the floor of each compartment beneath the liquid. Rising bubbles of gas are mixed thoroughly with the agitating liquid and become saturated with steam (and volatile organic species). As gas and wastewater are added to the reactor, its total pressure increases until it exceeds the desired maximum and a pressure-regulated valve is actuated. Each time the valve opens, steam (water-saturated gas and vapours) passes from the reactor through the vapour vent generally located in the rear.

All exiting gas (vapours and steam) are passed through the heat exchanger in which the vapours and steam are condensed. This vapour-phase condensate (VPC) is collected and sampled for each test.

7. LIQUID-PHASE EFFLUENT

The liquid-phase discharge from the reactor is a slurry of insoluble solids suspended in a liquor containing residual water-soluble organic matter as well as dissolved inorganic salts and acid. This liquid-phase slurry generally is referred to as the liquid-phase effluent (LP). It is depressurized by a separate liquid let-down system and collected in a storage tank.

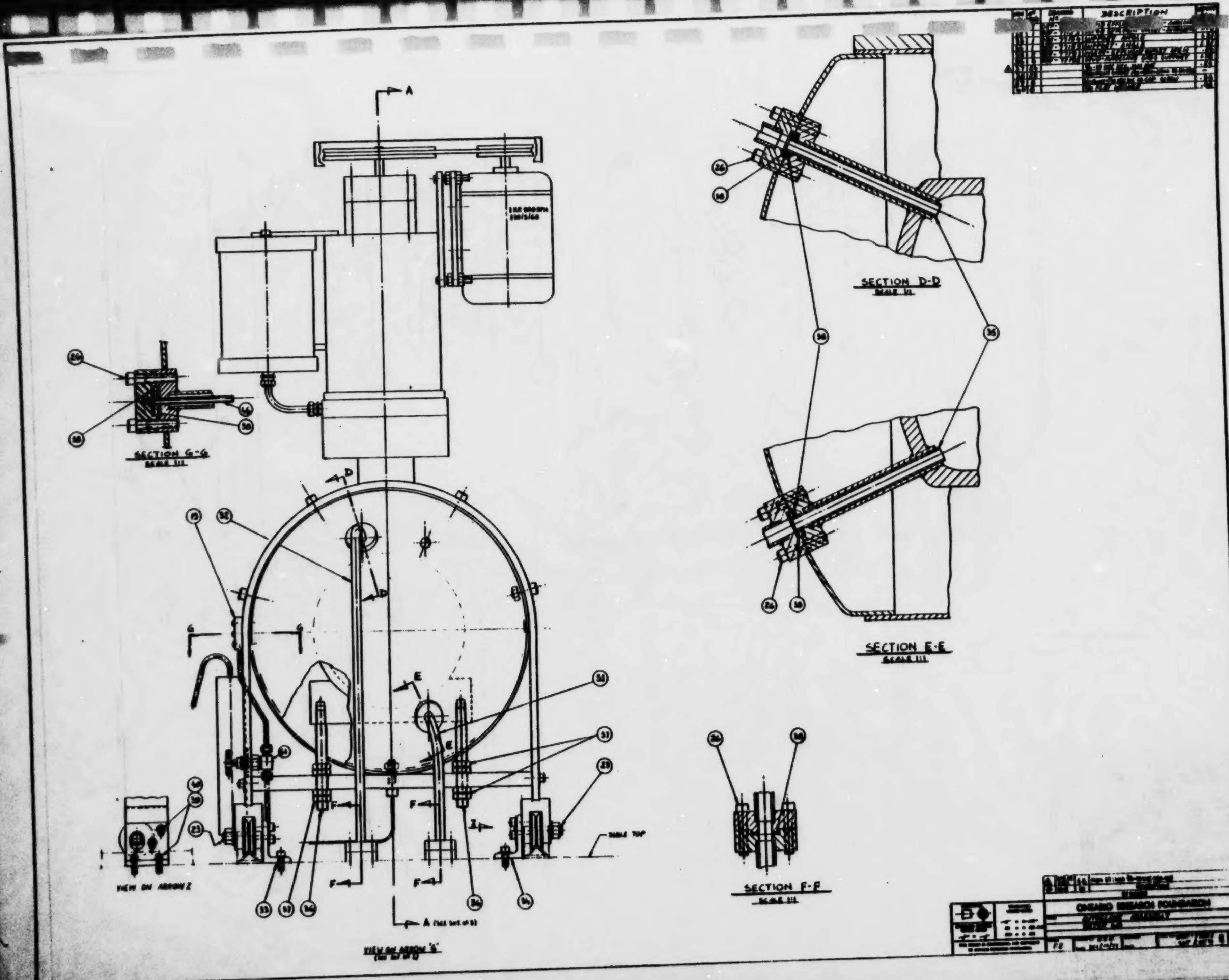
The liquid let-down system is activated by a conductivity probe located in the settling basin at the rear of the reactor adjacent to the fourth mixing compartment. Whenever the level of liquid in the settling basin rises above the probe, a ball-cock valve opens and liquid is forced out of the reactor. The liquid discharge from the autoclave passes through the tube-in-tube heat exchanger countercurrent to the flow of influent. Liquid enters the effluent storage tank at about 160°F.

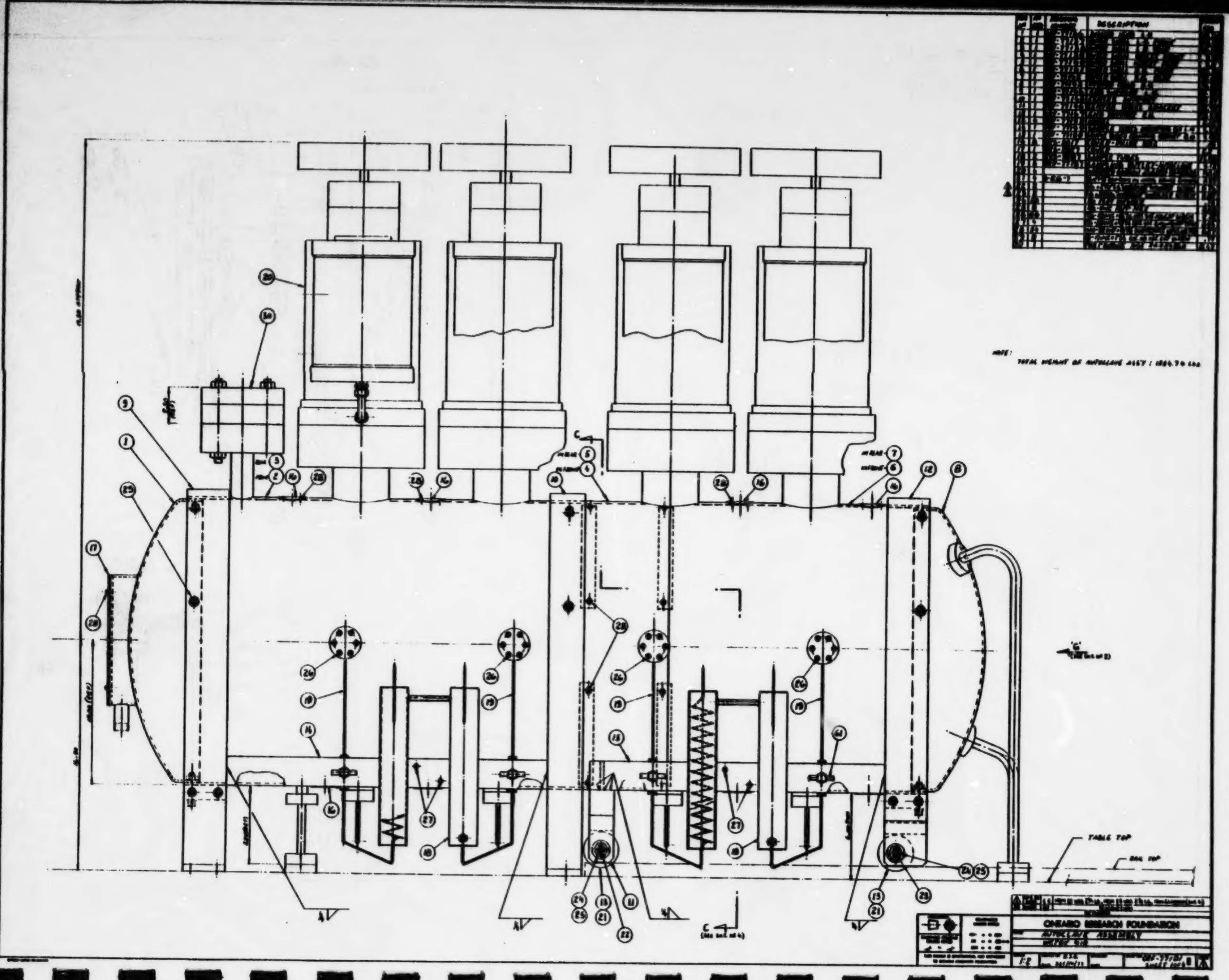
8. TEST PROCEDURE

The general test procedure includes the following steps:

- The reactor and agitator are pressurized.
- Fresh water is pumped into the reactor until the unit is filled.
- The heaters are then turned on and a small flow of air established to each compartment.
- After the reactor is at the desired temperature, waste is pumped at the desired rate through the heat exchanger and into the reactor. The air flow is adjusted accordingly. Steady-state temperatures throughout the process are generally achieved 60 to 90 minutes after pumping begins.
- The off-gas is monitored for oxygen concentration and adjustments to the oxidant flow made, if required.
- Feed is pumped for 2 to 3 reactor volumes (e.g. approximately 90 litres) to achieve steady-state concentrations throughout the process.
- Samples are then withdrawn from each compartment and from the feed, LPE and VPC.
- Temperatures and pressures are recorded throughout the process.

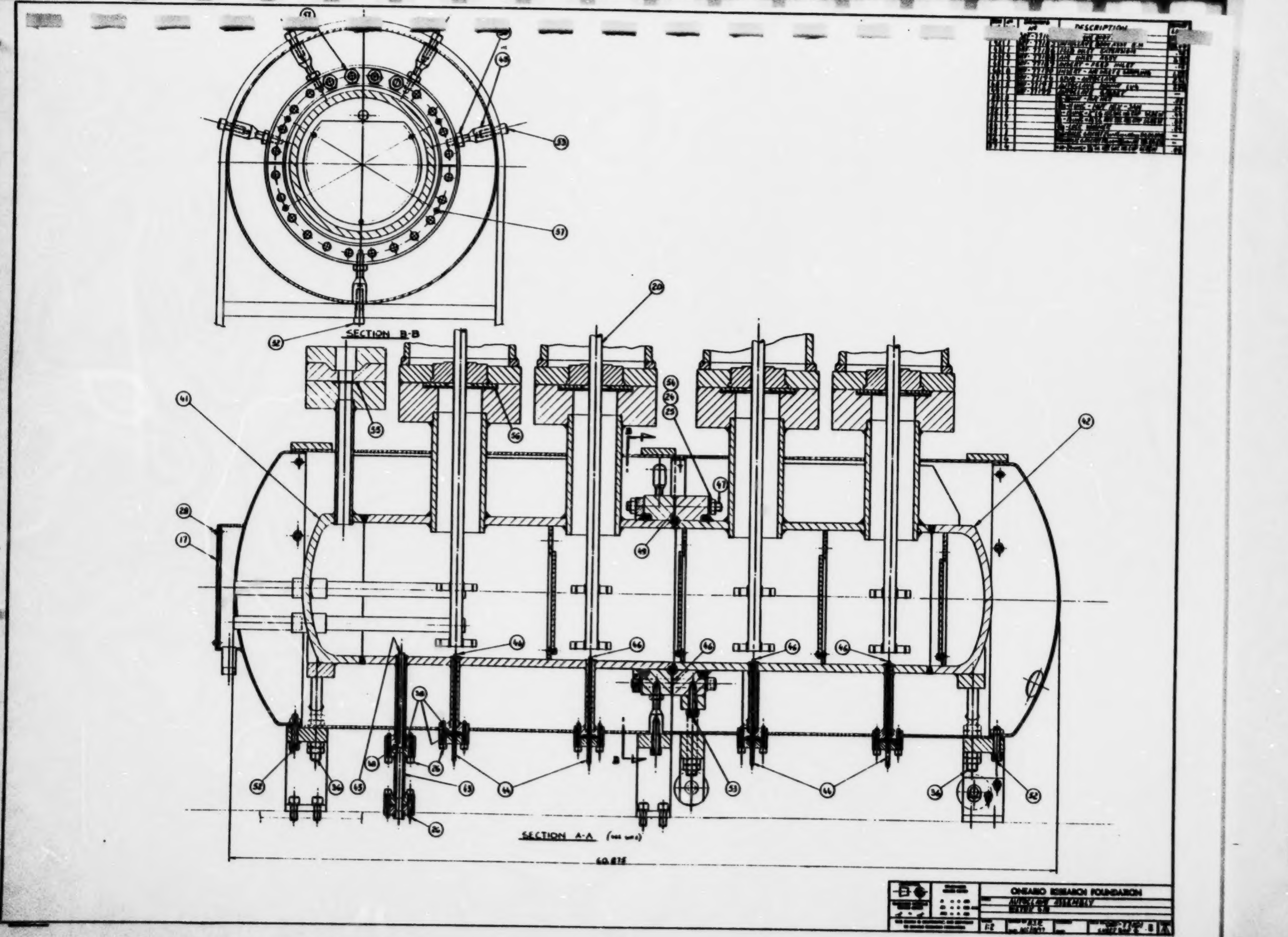
ONTARIORESEARCH
FOUNDATION
WETOX PROCESS
PILOT PLANT
sponsored by:
ONTARIO
OF IN
AND


DESCRIPTION
A
SECTION D-D
SCALE 1:1
SECTION E-E
SCALE 1:1
SECTION F-F
SCALE 1:1
SECTION G-G
SCALE 1:1
VIEW ON ARROW Z
VIEW ON ARROW 'A'
TABLE TOP
D
E
F
G
Z
26
38
36
35
44
15
32
31
37
23
29
14
33
34
ONTARIO RESEARCH FOUNDATION


DESCRIPTION
TABLE TOP
'G'
C
C
1
2
3
4
5
6
7
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30

NOTE:
TOTAL WEIGHT OF AUTOCLAVE ASS'Y : 1856.70 lbs

ONTARIO RESEARCH FOUNDATION
AUTOCLAVE ASSEMBLY


SECTION B-B
SECTION A-A
60.875
DESCRIPTION
ONTARIO RESEARCH FOUNDATION
AUTOCLAVE ASSEMBLY
51
48
33
57
32
41
55
56
20
54
24
25
47
49
42
28
17
44
46
38
26
63
58
34
53
52

APPENDIX D

Batch Test Conditions

Produced Water Test Conditions

Run #	Temp. (^oC)	Pressure (MPa)	Run Time (min)	Additions	Waste Code
PW-2 (Inj)	200	3.28	60	-	PW-1
PW-3	220	4.14	60	-	PW-1
PW-4	240	5.24	60	-	PW-1
PW-5	260	6.62	60	-	PW-1
PW-6	280	8.41	60	-	PW-1
PW-9	220	4.14	60	-	PW-2
PW-10	240	5.24	60	-	PW-2
PW-11	260	6.62	60	-	PW-2
PW-H	220	0.34 added at start	Heat up only	-	PW-1
PW-12 (Inj)	280	8.41	60	-	PW-1
PW-13 (Inj)	260	6.62	60	-	PW-1
PW-H2	220	0.34 added at start	Heat up only	5.0 g Bentonite	PW-1
PW-14	240	5.24	60	5.0 g Bentonite	PW-1
PW-15	260	6.62	60	5.0 g Bentonite	PW-1
PW-16	240	5.24	6	2.0 g Coke	PW-1
PW-17	280	8.41	60	5.0 g Bentonite	PW-1
PW-18	220	4.14	60	5.0 g Bentonite	PW-1
PW-19	240	5.24	60	1.0 g Bentonite	PW-1
PW-7	300	10.55	60	5.0 g Bentonite	PW-1
PW-20	220	4.14	60	5.0 g Bentonite + 0.25 g CuO	PW-1
PW-21	240	5.24	60	5.0 g Bentonite + 0.25 g CuO	PW-1
PW-22	260	6.62	60	5.0 g Bentonite + 0.35 g CuO	PW-1
PW-23	220	4.14	60	5.0 g Bentonite + H_2SO_4 to pH = 2.0	PW-1
PW-24	240	5.24	60	5.0 g Bentonite + H_2SO_4 to pH = 2.0	PW-1

Produced Water Test Conditions (Contd.)

Run #	Temp. (^oC)	Pressure (MPa)	Run Time (min)	Additions	Waste Code
PW-25	260	6.62	60	5.0 g Bentonite + H_2SO_4 to pH = 2.0	PW-1
PW-24 Repeat	240	5.24	60	5.0 g Bentonite + H_2SO_4 to pH = 2.0	PW-1
PW-26 (Inj)	240	5.24	30	5.0 g Bentonite	PW-1
PW-27 (Inj)	260	6.62	30	5.0 g Bentonite	PW-1
PW-28 (Inj)	280	8.41	30	5.0 g Bentonite	PW-1
PW-29 (Inj)	290	9.17	30	5.0 g Bentonite	PW-1
PW-30 (Inj)	240	5.24	30	5.0 g Bentonite + H_2SO_4 to pH = 2.0	PW-1
PW-31 (Inj)	240	5.24	30	5.0 g Bentonite + 0.25 g CuO	PW-1
PW-32	260	6.62	60	3.0 g Bentonite	CLPW Grease
PW-33	240	5.24	60	3.0 g Bentonite	CLPW Grease
PW-34	280	8.41	60	3.0 g Bentonite	CLPW Grease
PW-35	240	5.24	60		PW-1 Aqueous Phase
PW-36	260	6.62	60		PW-1 Aqueous Phase
PW-37	260	6.62	60	5.0 g Bentonite	PW-1 Aqueous Phase
PW-38	240	5.24	60		HTS
PW-39	240	5.24	90	2.0 g Suncor Coke (100 mesh) + 0.25 g CuO	HTS
PW-40	240	5.24	60	5.0 g Bentonite	HTS

Produced Water Test Conditions (Contd.)

Run #	Temp. (^oC)	Pressure (MPa)	Run Time (min)	Additions	Waste Code
PW-41	260	6.34	60	5.0 g Bentonite	HTS
PW-42	280	8.14	60	5.0 g Bentonite	HTS
PW-43	240	5.24	60	5.0 g Bentonite + 0.25 g CuO	HTS
PW-44	280	8.14	60	5.0 g Bentonite + 0.25 g CuO	HTS
PW-45	240	5.24	60	5.0 g Bentonite	P-34
PW-46	260	6.34	60	5.0 g Bentonite	P-34
PW-47	280	8.14	60	5.0 g Bentonite	P-34
PW-41 Repeat	260	6.34	60	5.0 g Bentonite	HTS
PW-42 Repeat	280	8.14	60	5.0 g Bentonite	HTS
PW-44 Repeat	280	8.14	60	5.0 g Bentonite + 0.25 g CuO	HTS
PW-47 Repeat	280	8.14	60	5.0 g Bentonite	P-34
PW-48	260	6.34	60	5.0 g Bentonite + 0.25 g CuO	HTS H_2O
PW-49	280	8.14	20	5.0 g Bentonite + 0.25 g CuO	HTS
PW-50	260	6.62	60	5.0 g Bentonite	HTS
PW-51	260	5.52	60	5.0 g Bentonite	HTS
PW-52	260	5.17	60	5.0 g Bentonite	HTS
PW-53	260	7.59	60	5.0 g Bentonite	HTS
PW-54	280	8.14	60	5.0 g Bentonite	HTS
PW-55	240	5.24	60	5.0 g Bentonite	CLPW
PW-56	260	6.34	60	5.0 g Bentonite	CLPW
PW-57	280	8.14	60	5.0 g Bentonite	CLPW
PW-55 Repeat	240	5.24	60	5.0 g Bentonite	CLPW
PW-56 Repeat	260	6.34	60	5.0 g Bentonite	CLPW
PW-57 Repeat	280	8.14	60	5.0 g Bentonite	CLPW

Delayed Coke Test Conditions

Run #	Temp. (°C)	Pressure (MPa)	Run Time (min)	Additions	Waste Code
AA-1	200	4.83	120		(-100 mesh)
AA-2	220	5.66	120		(-100 mesh)
AA-3	240	6.83	120		(-100 mesh)
AA-4	260	8.28	120		(-100 mesh)
AA-5	280	10.17	120		(-100 mesh)
AA-6	300	12.41	120		(-100 mesh)
C-1	240	4.83	150		(-100 mesh)
C-2	260	6.34	150		(-100 mesh)
C-3	280	8.14	150		(-100 mesh)
C-4	240	4.83	150	3.0 g NaOH	(-100 mesh)
C-5	260	6.34	150	3.0 g NaOH	(-100 mesh)
C-6	280	8.14	150	3.0 g NaOH	(-100 mesh)
C-7	200	3.03	150		(-100 mesh)
C-8	220	3.83	150		(-100 mesh)
C-9	200	3.03	150	3.0 g NaOH	(-100 mesh)
C-10	220	3.83	150	3.0 g NaOH	(-100 mesh)
C-11	200	3.03	150	1.0 g NaOH	(-100 mesh)
C-12	220	3.83	150	1.0 g NaOH	(-100 mesh)
C-13	240	4.93	150	1.0 g NaOH	(-100 mesh)
C-14	260	6.34	150	1.0 g NaOH	(-100 mesh)
C-15	280	8.14	150	1.0 g NaOH	(-100 mesh)
C-16	280	3.83	150	3.0 g H_2SO_4	(-100 mesh)
C-17	240	4.93	150	3.0 g H_2SO_4	(-100 mesh)
C-18	260	6.34	150	3.0 g H_2SO_4	(-100 mesh)
C-19	280	8.14	150	3.0 g H_2SO_4	(-100 mesh)
C-20	220	3.83	150	.25 g CuO	(-100 mesh)
C-16 (Repeat)	220	3.83	150	3.0 g H_2SO_4	(-100 mesh)
C-21	240	4.93	150	.25 g CuO	(-100 mesh)
C-22	260	6.34	150	.25 g CuO	(-100 mesh)
C-23 (Inj.)	200	3.03	150		(-100 mesh)
C-24 (Inj.)	220	3.83	150		(-100 mesh)
C-25 (Inj.)	240	4.93	150		(-100 mesh)
C-26	240	4.93	150		(+250 mesh)
C-27	260	6.34	150		(+250 mesh)
C-28	280	8.14	150		(+250 mesh)
C-29	300	10.34	150		(+250 mesh)

Delayed Coke Test Conditions (cont'd)

Run #	Temp. (°C)	Pressure (MPa)	Run Time (min)	Additions	Waste Code
C-30	290	9.17	150		(-100 mesh)
C-36	240	4.93	150		(-60 mesh)
C-37 (Inj.)	240	5.79	150		(-100 mesh)
C-38	260	6.34	90		(-60 mesh)
C-39 (Inj.)	260	7.24	150		(-100 mesh)
C-18 (Repeat)	260	6.34	150	3.0 g H_2SO_4	(-100 mesh)
C-26 (Repeat)	240	4.93	150		(-250 mesh)
C-8 (Repeat)	220	3.83	150		(-100 mesh)
C-40 (Inj.)	260	6.34	150		(-100 mesh)
C-41	280	8.14	150		(-250 mesh)
C-42	220	3.83	150		(-250 mesh)
C-43 (Inj.)	240	4.93	120	+.25 g CuO	(-100 mesh)
C-44 (Inj.)	240	4.93	120	+.40 g CuO	(-100 mesh)
C-45 (Inj.)	240	4.93	120	+.10 g CuO	(-100 mesh)
C-47	240	5.24	150	3.0 g NaOH	(-100 mesh)
C-48	240	5.24	150	3.0 g NaOH	(-100 mesh)
C-49	240	5.24	150		(-100 mesh)
C-50	240	5.24	150	+H_2SO_4 pH=2.0	(-100 mesh)
C-59 (Inj.)	260	6.34	150	+.05 g Alkaryl Sulfonate	(-100 mesh)
C-60 (Inj.)	260	6.34	150		(-100 mesh)
C-61	220 260	3.83 6.34	150		(-100 mesh)
C-74	260	6.34	150		(-100 mesh)
C-91	260	6.34	150	0.2 g NaOH	(-100 mesh)
C-100	260	5.52 air	90		(-100 mesh)
C-101	260	5.52	90		(-100 mesh)
C-96 (Inj.) (Repeat)	250	4.66	150	.25 g CuO	(-100 mesh)

Delayed Coke Test Conditions (cont'd)

Run #	Temp. (°C)	Pressure (MPa)	Run Time (min)	Additions	Waste Code
C-104	280	8.14	30		(-100 mesh)
C-103	260	6.34	60		(-100 mesh)
C-102	240	4.93	60		(-100 mesh)
C-106	280	8.14	120		(-100 mesh)
C-107	280	8.14	120		(-100 mesh)
C-113 (Inj.)	280	8.14	150		(-100 mesh)
C-114 (Inj.)	260	8.14	150		(-100 mesh)
C-115 (Inj.)	260	8.14	150		(-100 mesh)
C-116 (Inj.)	260	8.14	150	0.53 g Iron Powder +.05 g A. Sulfonate	(-100 mesh)

Fluid Coke Test Conditions

Run #	Temp. (°C)	Pressure (MPa)	Run Time (min)	Additions	Waste Code
C-31	240	4.93	150		(-100 mesh)
C-32	260	6.34	150		(-100 mesh)
C-33	280	8.14	150		(-100 mesh)
C-34	240	4.93	150	.25 g CuO	(-100 mesh)
C-35	240	4.93	150	H_2SO_4 pH=2.0	(-100 mesh)
C-31 (Inj.)	240	4.93	150		(-100 mesh)
(Repeat) C-32 (Inj.)	260	6.34	150		(-100 mesh)
(Repeat) C-33 (Inj.)	280	8.14	150		(-100 mesh)
(Repeat) C-46 (Inj.)	260	6.34	150		(-250 mesh)
C-51	220-260	3.83-6.34	150	.25 g CuO	(-100 mesh)
C-52	320	13.10	60		(-100 mesh)
C-53	320	13.10	60		(-100 mesh)
C-54	220-260	3.83-6.34	150		(-100 mesh)
C-55	100-260	0.34-6.34	180		(-100 mesh)
C-56 (Inj.)	260	6.34	150		(-100 mesh)
C-57	140-260	0.34-6.34	180		(-100 mesh)
C-58	180-260	0.34-6.34	180		(-100 mesh)
C-62 (Inj.)	260	6.34	150	+.05 g Alkaryl Sulfonate	(-100 mesh)
C-63 (Inj.)	280	8.14	150	+.05 g Alkaryl Sulfonate	(-100 mesh)
C-64	260	6.34	150	+.25 g CuO	(-100 mesh)
C-65	280	8.14	150	+.25 g CuO	(-100 mesh)
C-66-A (Inj.)	240	4.93	150		(-100 mesh)
C-67(Inj.)	220-240	3.83-4.93	150		(-100 mesh)
C-68(Inj.)	220-240	3.83-4.93	150	.25 g CuO	(-100 mesh)
C-69	280	8.10	150	.05 g Alkaryl Sulfonate	(-100 mesh)
C-66-B	240	4.93	150	.05 g Alkaryl Sulfonate	(-100 mesh)
C-71 (Inj.)	240	4.93	150	.05 g Alkaryl Sulfonate	(-100 mesh)

Fluid Coke Test Conditions (cont'd)

Run #	Temp. (°C)	Pressure (MPa)	Run Time (min)	Additions	Waste Code
C-72 (Inj.)	240	4.93	150	.25 g CuO .05 g Alk. Sulf.	(-100 mesh)
C-73	260	6.34	150	.25 g CuO	(-100 mesh)
C-75 (Inj.)	280	8.14	150	.05 g Alk. Sulf.	(-60 mesh)
C-76 (Inj.)	280	8.14	150	.25 g CuO .05 g Alk. Sulf.	(-60 mesh)
C-77 (Inj.)	260	6.34	150	.25 g CuO + .05 g Alk. Sulf.	(-60 mesh)
C-78 (Inj.)	260	6.34	150	.05 g Alk. Sulf.	(-60 mesh)
C-79 (Inj.)	240	4.93	150	.05 g Alk. Sulf.	
C-80 (Inj.)	240	4.93	150	.25 g CuO .05 Alk. Sulf.	(-60 mesh)
C-81 (Inj.)	240	4.93	150	.25 g CuO .05 Alk. Sulf.	(-60 mesh)
C-82 (Inj.)	240	4.93	150	.05 g Alk. Sulf.	(-60 mesh)
C-83 (Inj.)	260	6.34	150	.05 Alk. Sulf.	(-60 mesh)
C-84 (Inj.)	260	8.41	150	.05 g Alk. Sulf.	(-100 mesh)
C-85 (Inj.)	260	8.41	150	.5 g NaOH .05 g Alk. Sulf.	(-100 mesh)
C-86 (Inj.)	280	8.14	150	.25 g CuO .05 g Alk. Sulf.	(-60 mesh)
C-87 (Inj.)	260	6.34	150	.25 g CuO .05 g Alk. Sulf.	(-60 mesh)
C-88	280	8.14	150		(-100 mesh)
C-89 (Inj.)	260	6.34	150		(-250 mesh)
C-90 (Inj.)	240	4.93	150		(-250 mesh)
C-64 (Inj.) (Repeat)	260	6.34	150	+.25 g CuO	(-100 mesh)
C-65 (Inj.) (Repeat)	280	8.14	150	+.25 g CuO	(-100 mesh)
C-92 (Inj.)	280	8.14	150		(-250 mesh)

Fluid Coke Test Conditions (cont'd)

Run #	Temp. (°C)	Pressure (MPa)	Run Time (min)	Additions	Waste Code
C-82 (Inj.) (Repeat)	240	4.83	150	.05 g Alk. Sulf.	(-60 mesh)
C-93 (Inj.)	280	9.17	150	.05 g Alk. Sulf.	(-60 mesh)
C-72 (Inj.)	240	4.83	150	.25 g CuO .05 g Alk. Sulf.	(-100 mesh)
C-94 (Inj.)	250	5.52 Air	150	.25 g CuO .05 g Alk. Sulf.	(-100 mesh)
C-95 (Inj.)	250	5.52	150	.25 g CuO .05 g Alk. Sulf.	(-100 mesh)
C-96 (Inj.)	250	4.66	150	.25 g CuO .05 g Alk. Sulf.	(-100 mesh)
C-97 (Inj.)	250	4.66	150	.25 g CuO .05 g Alk. Sulf.	(-100 mesh)
C-94 (Inj.) (Repeat)	250	5.52 Air	150	.25 g CuO .05 g Alk. Sulf.	(-100 mesh)
C-98 (Inj.)	250	6.14	150	.25 g CuO .05 g Alk. Sulf.	(-100 mesh)
C-99 (Inj.)	250	7.34	150	.25 g CuO .05 g Alk. Sulf.	(-100 mesh)
C-96 (Inj.) (Repeat)	250	4.66	150	.25 g CuO .05 g Alk. Sulf.	(-100 mesh)
C-105 (Inj.)	280	8.14	150	.25 g CuO .05 g Alk. Sulf	(-100 mesh)
C-108	280	8.14	120		(-100 mesh)
C-109	280	8.14	120		(-100 mesh)
C-110 (Inj.)	240	5.24	150	.25 g CuO .05 g Alk. Sulf.	(-100 mesh)
C-111 (Inj.)	280	8.14	150	.25 g CuO .05 g Alk. Sulf.	(-100 mesh)
C-112 (Inj.)	280	8.14	150		(-60 mesh)
C-95 (Inj.)	250	5.52	150	.25 g CuO .05 g Alk. Sulf.	(-100 mesh)

Athabasca Pitch Test Conditions

Run #	Temp. (°C)	Pressure (MPa)	Run Time (min)	Additions	Waste Code
AP-1 (Inj.)	260	6.34	120		100 mesh
AP-2 (Inj.)	240	5.24	90		100 mesh
AP-3 (Inj.)	280	8.41	90		100 mesh
AP-4 (Inj.)	220	3.83	90		100 mesh
AP-5 (Inj.)	240	5.24	90	+.25 g CuO	100 mesh
AP-6 (Inj.)	240	5.24	90	H_2SO_4 to pH = 2.0	100 mesh
AP-7 (Inj.)	220	3.83	90		250 mesh
AP-8 (Inj.)	240	4.93	90		250 mesh
AP-9 (Inj.)	260	6.34	90		250 mesh
AP-10 (Inj.)	280	8.14	90		250 mesh
AP-11 (Inj.)	220	3.83	90	+.25 g CuO	100 mesh
AP-12 (Inj.)	260	6.34	90		100 mesh
AP-13 (Inj.)	240	4.93	120	.1 g CuO	100 mesh
AP-14 (Inj.)	240	4.83	120	.4 g CuO	100 mesh
AP-15 (Inj.)	240	4.93	120	.4 g CuO	100 mesh
AP-16 (Inj.)	260	6.34	120		100 mesh
AP-17 (Inj.)	220	3.83	90	.25 g CuO	100 mesh
AP-18 (Inj.)	280	8.14	90	.25 g CuO	100 mesh
AP-19 A	240	5.24	30		60 mesh
AP-19 B	240	5.24	60		60 mesh
AP-19 C	240	5.24	120		60 mesh
AP-20 A	260	6.34	30		60 mesh
AP-20 B	260	6.34	60		60 mesh
AP-20 C	260	6.34	120		60 mesh
AP-21 A	280	8.14	30		60 mesh
AP-21 B	280	8.14	60		60 mesh
AP-21 C	280	8.14	120		60 mesh
AP-22 (Inj.)	260	5.52	90		100 mesh
AP-23 (Inj.)	260	5.52 Air	90		100 mesh
AP-22 (Inj.) (Repeat)	260	5.52	90		100 mesh
AP-24 (Inj.)	240	4.83	90		250 mesh
AP-25 (Inj.)	260	6.34	90		100 mesh
AP-26 (Inj.)	280	8.14	90		100 mesh

Asphaltines Test Conditions

Run #	Temp. (^oC)	Pressure (MPa)	Run Time (min)	Additions	Waste Code
SYN-A-1 (Inj.)	280	8.14	120		SYNASH 100 mesh
SYN-A-2 (Inj.)	260	6.34	120		SYNASH 100 mesh
SYN-A-3 (Inj.)	240	5.24	120		SYNASH 100 mesh
SYN-A-4 (Inj.)	240	5.24	120	+.25 g CuO	SYNASH 100 mesh
SYN-A-5 (Inj.)	260	6.34	90	+.25 g CuO	SYNASH 100 mesh
SYN-A-6 (Inj.)	280	8.14	90	+.25 g CuO	SYNASH 100 mesh
A-5 (Inj.) (Repeat)	260	6.34	90	+.25 g CuO	SYNASH 100 mesh

Mixed Waste Test Conditions

Run #	Temp. (°C)	Pressure (MPa)	Run Time (min)	Additions	Waste Code
PMW-1	240	4.93	120	.05 g Alk. Sulf.	HTS H_2O + Syncrude 100 mesh
PMW-2	260	6.34	120	.05 g Alk. Sulf.	HTS H_2O + Syncrude 100 mesh
PMW-3	280	8.14	120	.05 g Alk. Sulf.	HTS H_2O + Syncrude 100 mesh
PMW-4	240	4.93	120	.25 g CuO	HTS H_2O + Syncrude 100 mesh
PMW-5	260	6.34	120	.25 g CuO	HTS H_2O + Syncrude 100 mesh
PMW-6	280	8.14	120	.25 g CuO	HTS H_2O + Syncrude 100 mesh
PMW-7	240	4.93	120		HTS H_2O + Suncor 100 mesh
PMW-8	260	6.34	120	.25 g CuO	HTS H_2O + Suncor 100 mesh
PMW-9	280	8.14	120	.25 g CuO	HTS H_2O + Suncor 100 mesh
PMW-10	240	4.93	120	+.25 g CuO	HTS H_2O + Suncor 100 mesh
PMW-11	260	6.34	120	+.25 g CuO	HTS H_2O + Suncor 100 mesh
PMW-12	280	8.14	120	+.25 g CuO	HTS H_2O + Suncor 100 mesh
PMW-13 (Inj.)	260	6.34	120		HTS H_2O + Syncrude 100 mesh

Mixed Waste Test Conditions (cont'd)

Run #	Temp. (°C)	Pressure (MPa)	Run Time (min)	Additions	Waste Code
PMW-14	240	4.93	120	.05 g Alk. Sulf.	HTS H_2O + Syncrude 100 mesh
PMW-15(Inj.)	240	4.93	120	.05 g Alk. Sulf.	HTS H_2O + Syncrude 100 mesh
PMW-16(Inj.)	240	4.93	120	.05 g Alk. Sulf	HTS H_2O + Syncrude 100 mesh
PMW-1 (Inj.) (Repeat)	240	4.93	120	.05 g Alk. Sulf.	HTS H_2O + Syncrude 100 mesh
PMW-3 (Inj.) (Repeat)	280	8.14	120	.05 g Alk. Sulf.	HTS H_2O + Syncrude 100 mesh
PMW-17(Inj.)	240	4.93	120	.05 g Alk. Sulf. .25 g CuO	HTS H_2O + Syncrude 100 mesh

APPENDIX E

4-10 Fluid Coke Discussion

Fluid Coke Pilot Plant Tests

Test 1

During the initial attempt to process the fluid coke in the four compartment continuous flow pilot plant, it was found that the coke was settling in both the pump housing and the inlet feed side of the heat exchanger.

This was difficult to detect because the pump continued to function and, via a loud call flowmeter, indicate that the proper amount of liquid was going into the reactor. After dismantling the pump and the connectors to the heat exchanger, it was found that, although these were blocked with coke, water was permeating through.

Test 2

In an attempt to overcome these problems prior to the second run, a few modifications were made. The feed liquid/coke was continuously recirculated through the pump suction housing. The resulting turbulence would prevent coke particle precipitation in this area.

Secondly, the pump was remounted so that it would be at the same elevation as the heat exchanger, thus helping to prevent any settling of the coke in the pump outlet to the heat exchanger line.

In addition, an air line was attached (with corresponding gas flowmeter) to the high pressure outlet end of the feed pump, further helping to minimize coke precipitation, due to increased pipe turbulence. Approximately 8 to 14 L/min of air was found to prevent most settling of the coke. (These modifications are shown in Figure 1).

After the second pilot plant test, higher conversion efficiencies were registered than could be accounted for on the basis of applied molecular oxygen alone. For example, 92% COD destruction (combined effluent) was calculated with only 28.6% oxygen consumption (operation data shown in Table 1a). It was apparent that the coke was still not getting into the reactor.

Test 3

In this test, a higher feed concentration was attempted, but with a lower feed liquid flowrate. The objective was to increase the system heat output in order that the reaction temperature could be increased.

Analysis of the samples from the test still showed higher conversion efficiencies than could be accounted for on the basis of supplied oxygen (operation data shown in Table 2a).

The sampling system on the unit is constructed using 0.25 inch (0.635 cm) valves and lines. It was felt that the actual concentration of 60 mesh coke was not coming through.

Test 4

The coke was subsequently ground to 100 mesh and tested for the fourth time in the pilot plant. Oxygen balances were double checked by taking gas bag samples. These samples were analyzed for CO_2, CO, total hydrocarbon, H_2, N_2 and O_2 by gas chromatography (operation data shown in Table 3a). Although the coke concentrations were found to correlate well with oxygen utilization and carbon dioxide production, it was apparent that larger amounts of coke were actually present in the vessel than should have been.

At this point, one of the agitators was removed and a significant layer of coke was found deposited about the circumference of the reactor compartment. It was apparent that, because of circumferential dispersion of the coke particles (due to specific gravity greater than water), the samples obtained for analysis had high concentrations of coke. (Sampling was not from the middle of the compartment, but at the wall of the compartment).

Test 5

This problem suggested that the flat blade turbine type impellers are not appropriate for relatively high specific gravity solid particles. Four pitched blade turbines were constructed, which would improve the axial dispersion of the coke particles. These were mounted at the low end of the agitator shaft, while flat blade impellers were mounted near the surface of the liquid.

To compare flow patterns of the different impeller types, a vessel, geometrically similar to one of the pilot plant's four compartments, was constructed and fitted with a transparent end cap. Observation of the flow patterns was made and included the following:

- the PBT showed a much less well defined particle distribution
- the PBT gave good axial dispersion with a high velocity at the bottom
- less vortexing was observed when using the PBT

- little axial gradient was observed when using the FBT and particles virtually stopped when out of the plane of the impellers' periphery.

Analysis from the ensuing trial indicated approximately 90% suspended solids reduction, yet approximately 24% oxygen consumption. Test conditions are given in Table 4a. It was apparent that the coke particles were still precipitating in the reactor compartments.

Test 6

At this point, it was concluded that higher coke oxidation rates would be necessary to reduce the precipitation problems. Batch testing indicated that oxygen partial pressure may be a limiting factor on the rate.

The continuous flow unit was thereafter modified to allow the introduction of pure oxygen instead of air.

After the sixth run, it was apparent that existing pilot scale equipment was not adequate for coke wet oxidation treatment, and further pilot plant testing was not justified.

TABLE 1a - Coke Slurry - 4-10 Unit

May 7, 1984

Waste Feed: 24 g/L 60 mesh Syncrude Coke + 0.83 g/L $CuSO_4$ + 0.05 g/L alkaryl sulfonate

Waste Pumping Rate: Water flow rate - 0.41 L/min
Calculated COD flow rate - 24.6 g/min

Reactor Residence Time: 87.8 minutes

Reactor Pressure: 4.83 MPa

Air Flow Rate:

Compartment	L/min
1	7.08
2	7.08
3	2.83
4	2.83
Heat Exchanger	14.15

Reactor Temperature Profile:

Compartment	Temperature (°C)
1	238
2	238
3	230
4	231
Mean Reactor Temperature	234

Water Balance: Measured Liquid Produced - 0.360 L/min
Measured Steam Produced - 0.050 L/min

Oxygen Balance: Measured Oxygen Concentration in Exhaust - 15.0%

Oxygen Consumed as Fraction of Supplied - 28.6%

Total Oxygen Consumed - 2.7 g/min

TABLE 2a - Coke Slurry - 4-10 Unit

May 16, 1984

Waste Feed: 34.1 g/L 60 mesh Syncrude Coke + 0.92 g/L $CuSO_4$ + 0.05 g/L alkaryl sulfonate

Waste Pumping Rate:
Water flow rate - 0.32 L/min
Calculated COD flow rate - 27.2 g/min

Reactor Residence Time: 112.5 minutes

Reactor Pressure: 4.83 MPa

Air Flow Rate:

Compartment	L/min
1	7.08
2	7.08
3	2.83
4	2.83
Heat Exchanger	14.15

Reactor Temperature Profile:

Compartment	Temperature (°C)
1	241
2	239
3	231
4	231
Mean Reactor Temperature	236

Water Balance:
Measured Liquid Produced - 0.235 L/min
Measured Steam Produced - 0.085 L/min

Oxygen Balance:
Measured Oxygen Concentration in Exhaust - 14.5%

Oxygen Consumed as Fraction of Supplied - 31.0%

Total Oxygen Consumed - 2.94 g/min

TABLE 3a - Coke Slurry - 4-10 Unit May 24, 1984

Waste Feed: 27.5g/L 100 mesh Syncrude Coke + 0.99 g/L $CuSO_4$ + 0.05 g/L alkaryl sulfonate

Waste Pumping Rate:
Water flow rate - 0.30 L/min
Calculated COD flow rate - 20.6 g/min

Reactor Residence Time: 120.0 minutes

Reactor Pressure: 4.83 MPa

Air Flow Rate:

Compartment	L/min
1	11.32
2	11.32
3	2.83
4	2.83
Heat Exchanger	28.30

Reactor Temperature Profile:

Compartment	Temperature (°C)
1	248
2	243
3	238
4	240
Mean Reactor Temperature	242

Water Balance:
Measured Liquid Produced - 0.17 L/min
Measured Steam Produced - 0.13 L/min

Oxygen Balance:
Measured Oxygen Concentration in Exhaust - 13.0%

Oxygen Consumed as Fraction of Supplied - 38.1%

Total Oxygen Consumed - 6.0 g/min

TABLE 4a - Coke Slurry - 4-10 Unit July 3, 1984

Waste Feed: 27.5 g/L 100 mesh Syncrude Coke + 0.99 g/L $CuSO_4$ + 0.05 g/L alkaryl sulfonate

Waste Pumping Rate:
Water flow rate - 0.29 L/min
Calculated COD flow rate - 19.9 g/min

Reactor Residence Time: 124.0 minutes

Reactor Pressure: 4.83 MPa

Air Flow Rate:

Compartment	L/min
1	16.98
2	14.50
3	2.83
4	2.83
Heat Exchanger	14.15

Reactor Temperature Profile:

Compartment	Temperature (°C)
1	248
2	244
3	242
4	238
Mean Reactor Temperature	243

Water Balance:
Measured Liquid Produced - 0.12 L/min
Measured Steam Produced - 0.17 L/min

Oxygen Balance:
Measured Oxygen Concentration in Exhaust - 16.0%

Oxygen Consumed as Fraction of Supplied - 23.8%

Total Oxygen Consumed - 3.4 g/min

TABLE 5a - Coke Slurry - 4-10 Unit

August 17, 1984

Waste Feed: 11 g/L 100 mesh Syncrude Coke + 0.99 g/L $CuSO_4$ + 0.05 g/L alkaryl sulfonate

Waste Pumping Rate:
Water flow rate - 0.425 L/min
Calculated COD flow rate - 11.7 g/min

Reactor Residence Time: 84.7 minutes

Reactor Pressure: 4.83 MPa

O_2 Flow Rate:

Compartment	L/min
1	8.49
2	1.98
3	0.85
4	0.57

Reactor Temperature Profile:

Compartment	Temperature (°C)
1	249
2	241
3	235
4	229
Mean Reactor Temperature	238.5

Water Balance:
Measured Liquid Produced - 0.400 L/min
Measured Steam Produced - 0.025 L/min

Oxygen Balance:
Measured Oxygen Concentration in Exhaust - 96%

Oxygen Consumed as Fraction of Supplied - 4%

Total Oxygen Consumed - 2.8 g/min

APPENDIX F

Letter to Phillips Petroleum

ONTARIO**RESEARCH**
FOUNDATION

SHERIDAN PARK RESEARCH COMMUNITY
MISSISSAUGA, ONTARIO, CANADA L5K 1B3 • (416) 822-4111 • TELEX 06-982311

CONFIDENTIAL May 2, 1984.

Dr. Floyd Farha,
Phillips Petroleum,
14C4 Phillips Building,
Bartlesville, Oklahoma 74004
U.S.A.

Dear Floyd:

With reference to our telephone conversation of April 30, please allow me to elaborate our needs.

May I also request confidentiality in our discussions or communications in this matter.

ORF undertakes research and development work for government and industry on a contract basis. We have, at present, a major contract with a Canadian client to develop a water treatment facility. I am involved with a process stream which contains residual refractory organic compounds (acetic, formic and some other carboxylic acids). The stream contains very little inorganic materials. We wish to destroy these organics to make the stream suitable for boiler feed water.

In literature investigations, we came upon Professor Smith's work and, eventually, to you. It appears that the catalyst systems you have developed and patented may be suitable for our needs.

As part of our programme, we will be developing a continuous pressure catalytic oxidation system on a laboratory scale. Construction of the apparatus is now almost completed and there remains the question of obtaining an effective catalyst. Our project will include a demonstration of technical feasibility with model (aqueous acetic acid) solutions followed by process waste streams. Kinetic and analytical parameters will be obtained. Following this, an economic assessment will be carried out with appropriate recommendations to the Client. Further work will then include pilot demonstrations and eventually full-scale plant work should the client choose to do so.

Contd....

Our immediate requirements are to obtain 10 lbs (20 lbs, if possible) of a commercially prepared catalyst. No analysis will be carried out or reported on the product, since our needs are only to produce a working demonstration. I would be very grateful if you could prepare a price quotation for this requirement, if, indeed, any is available. Perhaps you would be so kind as to indicate where we might obtain such a product if you do not have it in hand.

Thank you for your attention.

Yours very truly,

D. Lindsay Mulholland, Ph.D.
Associate Research Scientist
Environmental & Chemical
Engineering Division

DLM/id

APPENDIX G

Canada Patent Application

Petition and Appointment of Agent

The Patent Act

TO: THE COMMISSIONER OF PATENTS

(a) The Petition of ONTARIO RESEARCH FOUNDATION

whose full post office address(es) is (are) Sheridan Park Research Community, Mississauga, Ontario L5K 1B3

sheweth;—

(b) 1. That Herbert L. Robey

whose full post office address(es) is (are) Sheridan Park Research Community, Mississauga, Ontario L5K 1B3

made the invention entitled HIGH THERMAL FLUX DENSITY WET OXIDATION STEAM GENERATOR

which is described and claimed in the specification submitted herewith.

(c) 1a. That the entire right to obtain a patent for the said invention has been assigned to Your Petitioner(s).

2. That Your Petitioner(s) verily believe(s) that Your Petitioner(s) is (are) entitled to a patent for the said invention having regard to the provisions of the Patent Act.

(d) ~~2a. That this application is a division of application Serial Number filed~~

(e) 3. Your Petitioner(s) request(s) that this application be treated as entitled to the rights accorded by section 29 of the said Act having regard to the application(s) of which particulars are set out below, and represents that the said application(s) is (are) the first application(s) for patent for the said invention filed in any country which by treaty, convention or law affords similar rights to citizens of Canada by the inventor(s) or anyone claiming under him (them).

(f)

4. That Your Petitioner(s) hereby nominate(s) SIM & McBURNEY, who carries on business in Canada at the following address: Suite 701, 330 University Avenue, Toronto M5G 1R7, Canada, to be Your Petitioner's representative for the service of any proceedings taken under the Act.

5. That Your Petitioner(s) hereby appoint(s) SIM & McBURNEY, whose full post office address is Suite 701, 330 University Avenue, Toronto M5G 1R7, Canada, as Your Petitioner's agent, with full power to appoint an associate agent when required to do so by section 131 of the Patent Rules and to revoke such appointment, to sign the Petition and drawings, to amend the specification and drawings, to prosecute the application, and to receive the patent granted on the said application; and ratifies(y) any act done by the said appointee in respect of the said application.

6. Your Petitioner(s) therefore pray(s) that a patent may be granted to Your Petitioner(s) for the said invention.

SIGNED at Toronto, Ontario

this 25 day of January 1985

(g) ONTARIO RESEARCH FOUNDATION

Agents for applicant

(a) Here insert full name of applicant or applicants. (b) Here insert full first name, middle initial(s), full last name of inventor or inventors. If applicant is inventor, insert "Your Petitioner" or "Your Petitioners" as the case may be, and for address insert "as above". (c) Stroke out paragraph 1a *if applicant is inventor. (d) Complete for divisional application in names of same inventors as named in original application — otherwise stroke out. (e) Stroke out paragraph if Convention priority not claimed. (f) Here insert particulars of the application or applications upon which the claim for priority is based. (g) Signature of applicant or applicants. Execution by a company shall be by an officer of the Company; the officer's official capacity must be stated.*

No notarization or legalization necessary.

***If applicant is an assignee, assignment must be filed, preferably, but not necessarily, with the Petition.**

ASSIGNMENT

CANADA

(PATENT, PATENT APPLICATION)

In consideration of the sum of One Dollar ($1.00) and other good and valuable consideration, receipt of which is hereby acknowledged,

I, (We), Herbert L. Robey

(name(s) of assignor(s)*

assignor, whose full post office address (es) is (are) Sheridan Park Research Community,
Mississauga, Ontario L5K 1B3

do hereby confirm my (our) sale, assignment, transfer and setting over, and I (we) do hereby sell, assign, transfer and set over to

Ontario Research Foundation

(name of assignee)*

assignee, whose full post office address is Sheridan Park Research Community,
Mississauga, Ontario L5K 1B3

(A) my (our) entire right, title and interest for Canada in and to my (our) invention relating to and entitled

HIGH THERMAL FLUX DENSITY WET OXIDATION STEAM GENERATOR

(title of patent application as it appears in the Petition)

(i) as fully set forth and described in an application for Letters Patent of Canada to be filed under the above title and naming me (us) as inventor(s), the Petition for which was or will be executed on ______** or

(ii) as fully set forth and described in an application for Letters Patent of Canada filed under Serial No. on

together with my (our) entire right, title and interest in and to said application, any and all divisional applications thereof, and any and all Letters Patent of Canada which may issue or be re-issued for said invention to the full end of the term for which each said Letters Patent may be granted:

(B) my (our) entire right, title and interest in and to Canadian Patent No.
issued

AND I (we) hereby authorize the issuance to said assignee of any and all said Letters Patent not already issued as the assignee of my (our) entire right, title and interest in and to the same, for the sole use and benefit of said assignee, its successors, assigns or legal representatives.

AND I (we), on behalf of myself (ourselves) and my (our) executors and administrators, hereby covenant and agree to do all such lawful acts and things and to execute without further consideration such further lawful assignments, documents, assurances, applications, and other instruments as may reasonably be required by said assignee, its successors, assigns or legal representatives, to obtain any and all Letters Patent of Canada for said invention and vest the same in said assignee, its successors, assigns or legal representatives.

SIGNED at Mississauga, Ontario
(place of execution)

this 25 day of January 1985.

(signature(s) of assignor(s)) Herbert L. Robey

NB If assignor is a corporation, the seal of the corporation should be employed and the title of the signing officer should be specified.

STATEMENT BY WITNESS

I, John H. Woodley (name of witness), whose full post office address is 330 University Avenue, Toronto, Ontario, was personally present and did see

Herbert L. Robey

(name(s) of person(s) who signed assignment)

who is (are) known to me, execute the above assignment.

(signature of witness)

Instructions

Notarization and legalization not required.

* If name of an individual, given name to be spelled out in full. Names of assignor(s) and assignee should be the same in both the assignment and Petition, if any.

** Here insert the date of execution of the Petition, if any, if this date is known to the assignor(s) at the time of execution of the assignment.

Complete and return in triplicate to Sim & McBurney, Suite 701, 330 University Avenue, Toronto, Ontario, Canada M5G 1R7

HIGH THERMAL FLUX DENSITY WET OXIDATION STEAM GENERATOR

FIELD OF THE INVENTION

This invention relates to the wet air oxidation at elevated temperatures and pressures of organic matter in a liquid feed stream.

BACKGROUND OF THE INVENTION

Wet oxidation of organics at high pressures and temperatures has been predominantly used in the field of waste management for applications such as removing pollutants from organic processing installations, pulp and paper operations, milk processing operations and the like. U.K. patent specification 706,686 discloses a wet oxidation process adapted to the above uses and is additionally usable to generate steam energy from low grade powder coals by the wet oxidation of slurry coals. The process involves introducing to a reactor at high temperature and pressure a waste stream and air which are mixed within the reactor. The organics in the feed stream react with the oxygen in the air stream to produce mainly carbon dioxide and water. The reaction is exothermic with the consequent generation of heat. Providing the reaction is controlled, organics in a liquid feed stream can be oxidized to produce harmless products for discharge into the environment. Many additional techniques have been developed in the area of wet oxidation systems such as disclosed in U.K. Patent 812,832 and United States Patents 3,852,192; 3,920,548; 4,155,848; 4,174,280; 4,217,218 and 4,229,296.

The wet air oxidation of low grade solid fuels as proposed in U.K. Patent 706,686 is attractive because the world's high grade fossil fuels are gradually being depleted. The lower quality solid fuels, that is, those with higher sulfur and ash content are being used more widely for stationary thermal energy and electrical power generation. There are two major and costly problems associated with dry incineration of low grade fuels. The higher sulfur content of the fuel results in unacceptable sulfur dioxide emissions, and expensive and problematic flue gas desulfurization is required. Boilers tend to be more complex in dealing with the low quality solid fuels because continuous ash removal equipment must be used to handle the high volumes of ash generated during combustion. In the wet air oxidation of the low grade fuels the coal is slurried with water and pumped into a high temperature and high pressure reactor. Air or oxygen is injected continuously either into the feed line preceding the reactor or the reaction vessel. The oxygen reacts with the organic materials to produce carbon dioxide, water and heat. Advantages of wet air oxidation of the low grade fuels is that the sulfur is oxidized to sulfuric acid (or sulfate salts) and the ash is essentially solubilized in the acidic slurry. Heat of reaction is removed from the vessel in the steam and liquid effluents such as disclosed by the technique in U.K. Patent 706,686. The effluents can either be used directly or heat exchanged to produce clean steam.

The major difficulty with the approach disclosed in U.K. Patent 706,686 and many other of the above noted patents is that only very dilute fuel: water slurries can be tolerated due to physical-chemical equilibrium within the unit. The quantities of air and organics introduced to the reactor system must be monitored and controlled to avoid excessive temperature increases due to heat of combustion and avoid run-away reactions. The net result, therefore, is low energy recovery per unit volume of reactor vessel. Attempts have been made to provide a degree of control on the temperature of the reaction. United States patents 3,852,192 and 4,229,296 involve the use of heat exchangers in the primary reaction zone to provide for initial heat-up of the reactor system in the primary zone and to control subsequently to a limited degree the temperature in the primary reaction zone. However, both patents are directed to the treatment of the dilute fuel to water slurries which are well within the safety margin of avoiding a run-away reaction.

SUMMARY OF THE INVENTION

The process, according to this invention, provides for significantly increased energy recovery per unit volume of reactor vessel by operating the reactor in a manner which can treat significantly increased concentrations of organics in the feed stream.

The wet oxidation process is carried out at controlled high temperatures and high pressures for oxidizing organic matter dispersed in a liquid feed stream. The process comprises feeding the feed stream into a reactor system and introducing an oxygen containing gas into the system to oxidize the organic matter at the controlled high temperatures and pressures in the reactor system. The organic matter may be slurried, pulverized low grade coal or petroleum upgrading products such as coke or ptich. The oxygen-containing gas may be air, oxygen enriched air or oxygen. A vapor phase effluent is removed from the reactor system along with a liquid phase effluent, both of which contain the reaction products of oxidizing the organic matter in the feed stream. A humidity ratio under normal physical-chemical equilibrium operating conditions for the reactor system determines a flow rate of the oxygen containing gas, a rate of vapor phase effluent removal and an amount of the organic matter to be oxidized in the reactor system per unit of time for an energy balanced reactor system. According to this invention, the improvement comprises for a rate of vapor phase effluent in excess of a rate of vapor phase effluent production in the reactor system operating under normal physical-chemical equilibrium, introducing to the reactor system per unit of time significantly larger amounts of the organic matter and the oxygen containing gas. The energy produced from heat of combustion of the organic matter is in excess of energy in the reactor system which is removed in the vapor phase effluent and the liquid phase effluent. The excess energy is recovered from the reactor system via a heat exchange means independent of the feed stream, oxygen containing gas, vapor phase effluent and liquid phase effluent to maintain operation of the reactor system at the controlled high temperatures and pressures while operating the reactor system outside of the normal physical-chemical equilibrium conditions. This provides significant higher energy recovery per unit volume of reactor system.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are shown in the drawings wherein:

Figure 1 is a schematic process flow diagram showing the reactor system in which a preferred embodiment of the inventive process is carried out.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In conventional wet oxidation processes, heat removal from the system is determined by the quantity of heat that can be removed in the vapor phase effluent and the liquid phase effluent. In operating a reactor system within the normal physical-chemical equilibrium operating conditions, the maximum amount of organic matter and air introduced into the system is thereby determined. Knowing the rate of oxidation of the organics for a given feed stream and the energy produced by the heat of combustion, the amount of organics in the feed stream has to the controlled to ensure that temperature does not begin to elevate to extent that the auto thermal reaction moves into a run-away condition. This has been readily accomplished in the past by the processes disclosed in the above noted patents.

According to this invention, it has been determined that by a modification in the process of running the wet oxidation reactor system, the specific organic matter concentration in the feed stream can be significantly increased. According to this invention, there are two determinative factors to be considered in operating the reactor system in a condition which would normally result in a run-away reaction. The first to be considered is the humidity ratio which is the mass of steam contained per unit mass of oxidizing gas. The humidity ratio is a function of temperature and total pressure. The humidity ratio determines the amount of moisture that can be contained in the vapor phase effluent. Knowing the humidity ratio and assuming a certain vapor production rate, the air flow rate and hence the fuel concentration can be calculated. The humidity ratio is calculated as follows:

$$HR = \frac{\text{mol.wt. of water}}{\text{mol.wt. of gas}} \times \frac{A}{B-A} \qquad I$$

wherein:
- i) mol. wt. is molecular weight;
- ii) A is the partial pressure of water vapor at the temperature of the reactor;
- iii) B is the total pressure of the system; and
- iv) HR = humidity ratio (wt steam/wt gas)

The second factor to be considered in operating the reactor system according to this invention, is the energy production. Normally the energy entering and produced within the process cannot exceed the energy removed in the liquid and vapor effluents. If this balance is not effective, the temperature of the reactor can rise to a run-away condition. By selective manipulation of the process controllable variables, including temperature and pressure, energy production within the system can be increased to improve significantly the energy recovery per unit volume of reactor system.

The specific fuel concentration in the feed stream, that is organic matter concentration, if it is significantly increased and there is sufficient oxidizing gas present, the impact on the system will be that the heat output will correspondingly increase. According to this invention, the excess energy generated is recovered from the reactor system in a manner to maintain the desired elevated temperatures and pressures in the reactor system, yet avoid run-away reaction conditions.

In a normal wet oxidation system operating within safe ranges, the limits with respect to the concentration of organic matter in the feed stream can be explained with reference to Figure 1. Based on the developments in the prior art wet oxidation systems, the behavior of the system can be reasonably predicted by humidity ratio and energy balance calculations. For a reactor temperature of approximataly 300°C and a total pressure in the range of 14 MPa (Mega Pascals) wherein heat losses are negligible, the following calculations are made to arrive at the upper limit of organic matter concentration in the feed stream. The allowable fuel concentration, i.e., concentration of organic matter in the feed stream, is a function of the humidity ratio and the process energy balances. Assuming air as the oxidant, the humidity ratio becomes:

$$HR = 0.99 \frac{\text{kg steam}}{\text{kg air}} \qquad \text{II}$$

Assuming for complete combustion, that 2.5 kg of oxygen per kg of solid fuel is required and knowing that there is 0.2314 kg of oxygen per kg of air, then the humidity ratio of formula II becomes:

$$HR = 10.7 \frac{\text{kg steam}}{\text{kg solid fuel}} \qquad \text{III}$$

The second determinant in operating the reactor system is to maintain an energy balance, which is developed as follows:

$$E_C + E_F = E_V + E_L + E_E \qquad \text{IV}$$

wherein

E_C = the heat of combustion

E_F = heat contained in liquid feed to reactor

E_V = heat removed in the vapor phase effluent

E_L = heat removed in the liquid phase effluent

E_E = excess energy remaining in the reactor system not removed in the vapor and liquid phase effluents

The energy balance may be expressed as follows:

$$m_f \times H_c \times e + m_f \times C_p \times T_F = H_{ST} \times m_V + m_L \times C_p \times T_R + E_E \qquad \text{V}$$

wherein

m_f = mass flow rate of fuel (kg/time unit)
H_c = heating value of fuel (MJ/kg)
e = oxidation efficiency
m_f = mass flow rate of feed liquid (kg/time unit)
T_F = feed temperature (°C)
m_V = mass flow rate of VPE (kg/time unit)
m_L = mass flow rate of LPE (kg/time unit)
T_R = reaction temperature (°C)
E_E = excess heat produced during reaction, which exceeds VPE + LPE removal limits
VPE = vapour phase effluent
LPE = liquid phase effluent
C_p = specifc heat of water
H_{ST} = enthalpy of steam

Providing for:

m_F = 100 kg/time unit
H_c = 35 MJ/kg
e = 0.9
T_F = 50°C
T_R = 300°C
E_E = 0
$C_p \simeq 0.0044$ MJ/kg/°C
$H_{ST} \simeq 2.5$ MJ/kg

and knowing:

$m_L = m_f - m_V$

the above equation reduced to two unkowns:

$$31.5\ m_f = 1.18\ m_V = 110\ \text{MJ/kg of liquid}$$

or

$$31.5\ \text{MJ} = \frac{1.18\ m_V}{m_f} + \frac{110}{m_f} \qquad \text{VI}$$

Knowing that $HR = \frac{m_V}{m_f}$

and substituting into equation VI, the solution is

m_f = 5.82 kg/time unit
m_V = 62.4 kg/time unit
m_L = 36.7 kg/time unit

For the above analyzed system operating under normal conditions in maintaining the physical-chemical equilibrium in the reactor system, the feed includes a concentration of 5.82% by weight of organics with a mass flow rate of vapor effluent of 62.4% by weight. By introducing the features of this invention, the effectiveness of the reactor system can be considerably increased.

The humidity ratio does not change because the humidity ratio is based on parameters which remain the same in either the prior art systems or the systems according to this invention. The energy balance is modified, however, because E_E, the excess heat generated is not known. Therefore, equation V becomes:

$$31.5 = \frac{1.18\, m_v}{m_f} + \frac{110}{m_f} + \frac{E_E}{m_f} \qquad \text{VII}$$

Providing for a vapor phase effluent of 80% by weight of the feed flow rate, direct substitution of this value into the humidity ratio expression provides a solid fuel weight of 7.48% by weight per time unit. Substituting this value for m_f in the above equation VII solve, E_E equals 31.2 MJ per unit of time. To maintain reactor temperature and prevent a run-away condition in the reactor system, 31.2 MJ per unit of time is recovered from the unit. As shown in Figure 1, a heat exchanger is provided in the reactor system to recover the excess heat from the reactor to provide for a controlled reaction even though the parameters are normally outside of the physical-chemical equilibrium operating conditions for the reactor system. The heat exchanger includes a cooling coil where heat exchange medium flows through the coil to recover heat from the reactor system and maintain the temperature of the reaction at the desired level of approximately 300°C. The heat recovery fluid may be cooling water or oil which removes the excess energy from the reaction system. The flow rate of the heat recovery fluid is determined by the desired temperature for the reaction. As the temperature in the reactor system is monitored, a controller controls a valve or the like in the heat exchanger coil to either increase or decrease the flow rate of the heat recovery fluid depending upon the corresponding increase or decrease of monitored reactor temperature. In this manner, the reactor temperature is maintained fairly constant at the desired level of 300°C. Should boiler feed water be used as the heat recovery fluid in the heat exchanger, the water, after having passed through the heat exchange coil, is flashed into steam. The steam may then be used for electrical power generation or for space and/or process heating requirements.

The total heat output for the normal system with the balanced physical-chemical equilibrium operating conditions provides total energy output which is the sum of E_V plus E_L which equals 203.7 MJ per unit of time. Compared to this, the total heat output of the system, according to this invention, is 261.8 MJ per unit of time which is the sum of E_V plus E_L plus E_E. Therefore, the process according to this invention can provide considerably greater heat output per unit volume of reactor. The vapor phase production rate is considerably higher, according to this invention, which is 80% by weight compared to the 62.4% by weight of the normal system which is an increase of approximately 28% for the particular embodiment discussed. In the production of greater quantities of vapor phase effluent and considering that the wet oxidation reaction occurs in the liquid phase, greater residence time in the liquid phase is obtained within the reactor. According to this invention, to realize the same heat output compared to a conventional wet oxidation system, the reactor system would be approximately one-half the size of the conventional unit. The heat exchange coils within the reactor system would occupy a small volume within the reactor due to the rapid heat of transfer caused by the turbulent environment within the reactor system.

Accordingly, the process of this invention can treat organic matter concentration in the feed stream ranging from 5% to 30% by weight. For example, with 60 to 90% by weight vapor phase effluent and 10 to 40% by weight liquid phase effluent, these above concentration ranges for the organic matter may be treated in the feed stream. The reactor system temperatures are preferably in the range of 170°C to 340°C and pressures of 5 to 21 MPa.

Considering the use of the wet oxidation reactor system, according to this invention, for in situ oil recovery, the energy of the vapor phase effluent is used as follows. Production of high temperature water approximately 280°C can be accomplished. The high temperature water can be passed through a steam generator for high pressure steam production. Assuming 280°C water and 80% quality injection steam desired for high pressure steam injection in oil recovery, about 60% of the total enthalpy necessary is contained as a sensible heat in the high temperature water. Therefore, fossil fuel operating costs and steam generator size would be correspondingly decreased in accordance with this invention. Production of low pressure, approximately 6.4 MPa process steam is available from the reactor system for on site electrical generation or heat requirements.

It is appreciated that from the separator even higher steam production can be achieved although normally the production would not exceed 95% of the water feed.

The reactor may be a multi-stage device such as disclosed in U.S. Patent 3,920,548. Within each compartment, a heat exchange coil is used. A control valve is provided for each coil in the respective compartment. By monitoring the temperature in each compartment, the flow rate of heat recovery fluid may be varied to maintain the temperature in that compartment within the desired operating range which may be permitted to fluctuate between 270°C to 300°C. The heat recovery fluid from each of the heat exchangers of the compartments is then processed in accordance with the standard techniques to recover the energy from the fluid for purposes of generating power or heating.

The advantages of this wet oxidation system which provides for greater heat production from the unit size of reactor is that all sulfur in the low grade fuels is converted to soluble sulfates thereby eliminating sulfur dioxide emission associated with dry combustion techniques in standard thermogenerating systems. The metals contained in the solid fuel are solubilized and concentrated by a factor of up to 10 and therefore provide potential recoverable resources. High energy efficiencies are realized due to energy being released in the liquid phase or by direct evaporation. In accordance with this invention more of the effluent exiting the system as steam can be reused directly as a steam source or can be condensed for reuse as a reasonably clean water source, which is suitable for the aforementioned in situ oil sands recovery applications.

Although preferred embodiments of the invention have been described herein in detail, it will be understood by those skilled in the art, that variations may be made thereto without departing from the spirit of the invention or the scope of the appended claims.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. In a wet air oxidation process at controlled high temperatures and high pressures for oxidizing organic matter dispersed in a liquid feed stream comprising feeding said feed stream into a reactor system and introducing an oxygen containing gas into said system to oxidize said organic matter at said controlled high temperatures and pressures in said reactor system, removing from said reactor system a vapor phase effluent and a liquid phase effluent which contain the reaction products of oxidizing said organic matter in said feed stream, a humidity ratio under normal physical-chemical equilibrium operating condition for said reactor system determining a flow rate of said oxygen containing gas, a rate of vapor phase effluent removal and an amount of said organic matter to be oxidized in said reactor system per unit of time for an energy balanced reactor, the improvement comprising for a rate of said vapor phase effluent from said reactor in excess of a rate of vapor phase effluent from said reactor system operating under normal physical-chemical equilibrium, introducing to said reactor system per unit of time significantly larger amounts of said organic matter and said oxygen-containing gas to produce thereby energy from heat of combustion of said organic matter which is in excess of energy in said reactor system which is removed in said vapor phase effluent and said liquid phase effluent, recovering said excess energy from said reactor system via a heat exchanger means independent of said feed stream, oxygen-containing gas, vapor phase effluent and liquid phase effluent to maintain operation of said reactor system at said controlled high temperatures and pressures while operating said reactor system outside of said normal physical-chemical equilibrium operating conditions

to provide significantly higher energy recovery per unit volume of reactor system.

2. In a process of claim 1, said feed stream having concentrations of organics in the range of 5% to 30% by weight of said organic matter per unit weight of said feed stream.

3. In a process of claim 1, said oxygen-containing gas being selected from the group of gases consisting of air, oxygen enriched air and oxygen.

4. In a process of claim 2, said organic matter being pulverized low grade coal.

5. In a process of claim 2, said organic matter being petroleum upgrading by-products.

6. In a process of claim 1, said controlled temperature ranging from 170° to 340°C and said controlled pressure ranging from 5 to 21 MPa.

7. In a process of claim 2, for 100 units of said feed stream per unit of time, 60 to 90 units of vapor phase effluent and 10 to 40 units of liquid phase effluent are produced per unit of time.

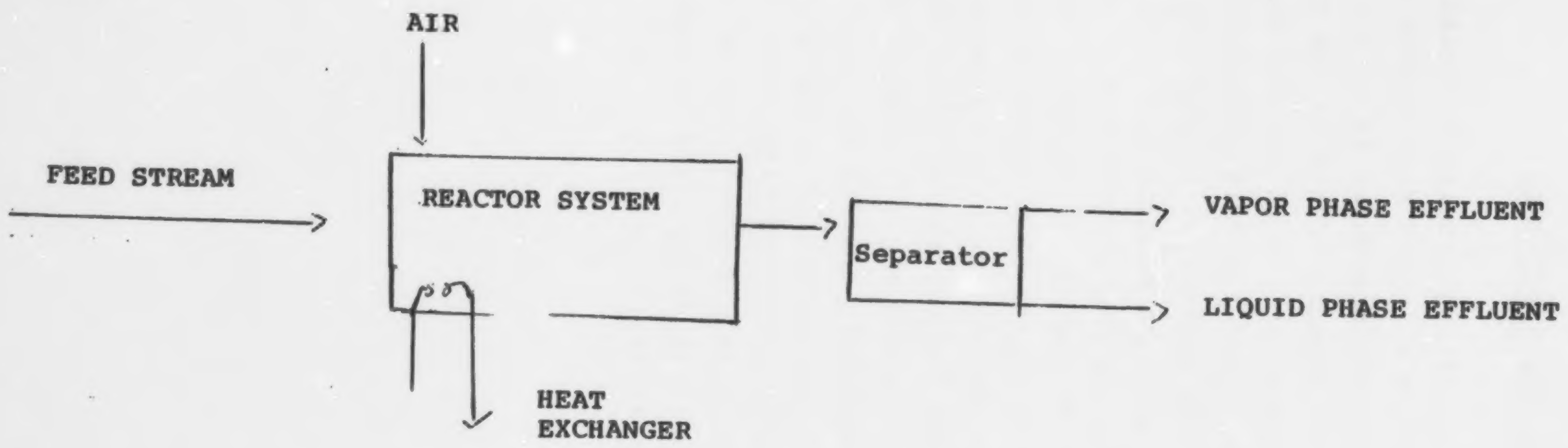
8. In a process of claim 1, said heat exchanger means being a heat exchange coil placed in said reactor system, passing a medium through said coil at a rate to recover said excess energy in the form of heat from said reactor system.

9. In a process of claim 7, said combustion of said organics is approximately 90% efficient.

ABSTRACT OF THE DISCLOSURE

A wet air oxidation process for oxidizing organic matter dispersed in a liquid feed stream at controlled high temperatures and pressures is capable of treating concentrations of organic matter in the feed stream far in excess of concentrations of organic matter treated in the normal type of wet air oxidation process. The improvement in the process is in the provision of a vapor phase effluent from the reactor system which is considerably greater than normal due to the introduction of high volumes of the oxidizing gas. This provides for increased concentrations of organic matter in the feed stream; however, resulting in the generation of excess energy within the reactor system which cannot be removed in the vapor and liquid phase effluents from the reactor system. The process is adapted to recover this excess energy from the reactor system to permit the reactor system to continue operating within the controlled high temperatures and high pressures, yet well outside of the normal physical-chemical equilibrium operating conditions for the reactor system.

FIGURE 1


AIR
FEED STREAM
REACTOR SYSTEM
Separator
VAPOR PHASE EFFLUENT
LIQUID PHASE EFFLUENT
HEAT
EXCHANGER

APPENDIX H

Computer Program Listing

```
C      SOLID FUEL WET OXIDATION STEAM GENERATOR
C
C
C      Program to evaluate the technical and economic feasibility of
C      using the Wetox Process to generate steam through the combust-
*C     ion of low grade solid fuels (eg.high sulfur petroleum coke).
C      A patented feature has been incorporated, which permits high
C      energy recoveries per unit reactor volume.
C      There are six options as follows:
C
C      OPT1-Air sys.,credit given for 'coil' hot water (after heat
            exchange). VPE steam for direct injection- cost=?
C
C      OPT2-Air sys.,credit given for 'coil' LP steam . VPE steam for
            direct injection - cost =?
C
C      OPT3-Air sys.,VPE heat exchanged for high press. hot water. 'Co
            + VPE HW' added together. Total cost of hot water =?
C
C      OPT4-O2 sys.,credit given for 'coil' hot water (after heat
            exchange). VPE steam for direct injection - cost =?
C
C      OPT5-O2 sys.,credit given for 'coil' LP steam. VPE steam for
            direct injection - cost =?


C
C      OPT6-O2 sys.,VPE heat exchanged for high press. hot water, credi
            given for CO2 recovered. 'Coil + VPE HW' combined. Total
            cost of hot water =?
C
C      Open remote data files and read in variables.
C
        OPEN(1,FILE='DATA1')
        READ(1,900)OXIDF,FF,EA,R,CODRED,CN,HEATOUT,RECEFF,AMATL,DENS,CCF
       OPEN(2,FILE='DATA2')
       READ(2,910)CKWHR,CF,ALIME,ANAOH,CRF,CH4,STM,HW,ST,CO2,OPT,FMAX
   910 FORMAT(12F16.4)
   900 FORMAT(11F16.4)
       WRITE(*,940)HEATOUT,OPT
   940 FORMAT(9X,///,' WETOX HEAT OUTPUT(MJ/H)='F8.0,9X,'OPTION ',F2.0,/

       WRITE(*,930)OXIDF,CN,AMATL
   930 FORMAT(6X,'O2 CONC='F6.4,6X,'#COMP='F2.0,6X,'TIT GR='F4.0,/)
       WRITE(*,900)OXIDF,FF,EA,R,CODRED,CN,HEATOUT,RECEFF,AMATL,DENS,CCF
       WRITE(*,910)CKWHR,CF,ALIME,ANAOH,CRF,CH4,STM,HW,ST,CO2,OPT,FMAX
       TCR=250.
C
C      Reactor temperature do loop.
C
```

```
C
      DO 100 I=1,7
      VPFR=.4
      TCR=TCR+10
C
C     Vapour:feed ratio do loop.
C
      DO 200 J=1,5
      VPFR=VPFR+.1
      VAPP=2.77E+4*EXP(-4628.6/(273.+TCR))
      REACP=VAPP+1.7/OXIDF
C
C     Reactor pressure do loop.
C
      DO 300 K=1,5
      IF(REACP.GT.17.5)GOTO 290
      IF(OPT.EQ.3.)GOTO 14
      IF(OPT.EQ.6.)GOTO 14
      IF(REACP.LT.13.8)GOTO 290
   14 CONTINUE
C
C     Calculate Wetox process design parameters.
c


      HR=.622*(VAPP/(REACP-VAPP))
      FUEL=(VPFR/HR/2.5)*OXIDF
      IF(FUEL.GT.FMAX)GOTO 290
      RATE=FF*EXP(-EA/R/(TCR+273.))
      CODREM=1.-CODRED
      TIME=(EXP(-LOG(CODREM)/CN)-1.)/RATE*CN+10.
      FEEDRAT=HEATOUT/FUEL/CODRED/RECEFF/2088.
      CO2P=FUEL*FEEDRAT*.8*CODRED*1440.*3.7
      RN=1.
      TOTTVOL=0.
      DUMMY=0.
C
C     Reactor(s) size calculations,dimensions,wall thickness etc.
C
   13 VOLRA=FEEDRAT*TIME*(1.-VPFR)*1.2/RN
   12 VOLRT=VOLRA*1.5/1000.+TOTTVOL
      DIA=(VOLRT/3.146/CN*4.)**.33
      IF(DIA.LE.1.7)GOTO 11
      RN=RN+1
      GOTO 13
   11  ENGTH=DIA*CN
      DUMMY=DUMMY+1.
      WALLTH=REACP*DIA*50./(124.-.6*REACP)
```

```fortran
      WTMET=DENS*DIA*31.46*1.2500*(ENGTH+.5*DIA)
      WTSTEL=7.84*DIA*3.146*WALLTH*(ENGTH+.5*DIA)
      STEEL=78.*(WTSTEL**(-.38))*WTSTEL*RN
C
C     Reactor energy balances.
C
      QLPE=(1.-VPFR)*FEEDRAT
      QVPE=VPFR*FEEDRAT
      HLPE=QLPE*TCR*.0044
      HVPE=QVPE*2.5
      HLPEHR=HLPE*60.
C
C     Calculate heat which must be removed using internal coils.
C
      HEXC=HEATOUT/60.-HLPE-HVPE
      HEXCT=HEXC*60.
      CCH4=0.
      EXTHEAT=0.
      TDIA=0.
      TUBEL=0.
      CVAL=0.
      CWFL=0.
      IF(HEXC.LT.0)GOTO 25


C
C     Calculate internal cooling coil size specifications
C
      CWFL=HEXC/2.5/RN
      REDN1=1.-(1./(1.+RATE*TIME/CN))
      CWCOIL1=CWFL*REDN1
      TDIA=(CWCOIL1/3.146/4.5)**.5
      ALMTD=30.-(TCR-20.)/ALOG(30./(TCR-20.))
      TUBEL=HEXC*REDN1/(10.2E-6*ALMTD*TDIA*314.6)
      TUBEWT=.43*TUBEL/REDN1
      TUBEVOL=TUBEL*3.146*(TDIA+.6)**2./4./10000.
      TOTTVOL=TUBEVOL/REDN1
      IF(DUMMY.GT.1.)GOTO 26
      REAVT=TOTTVOL+VOLTR
C
C     Determine credit to be given for 'coil' product.
C
      CVAL=HW*(HEXC+HLPE)*475.2
      IF(OPT.EQ.2.)CVAL=ST*(HEXC+HLPE)*475.2
      IF(OPT.EQ.5.)CVAL=ST*(HEXC+HLPE)*475.2
      IF(OPT.EQ.3.)CVAL=0.
      IF(OPT.EQ.6.)CVAL=0.
      VOLTEX=1.1*VOLRT
      IF(REAVT.LT.VOLTEX)GOTO 26
      GOTO 12
C
C     If excess energy is negative, calculate energy required to
C     sustain reaction, and cost assuming natural gas fuel.
   25 EXTHEAT=HEXC*(-1.)*60.
      TUBEWT=0.
      CCH4=EXTHEAT*CH4*7920.
   26 continue
C
C     Calculate practical length of internal cooling coil.
C
      COILL=2.*DIA*DIA*3.146/((TDIA+1.)/100.)*CCF
C
C     Oxygen or air flows and compressor duty req'd.
C
      QOXY=FUEL*FEEDRAT*2.5
      S=3.
      IF(REACP.GE.7.)S=4.
      IF(OXIDF.EQ..2314)GOTO 30
      QGAS=QOXY/.00143
      GOTO 40
   30 QGAS=QOXY*3600.
   40 CONTINUE
      COMPHP=.008*S*QGAS*(((REACP+.7)/.1)**(.286/S)-1.)
      COMPKW=.746*COMPHP
      IF(AMATL.EQ.7.)GOTO 50
      IF(AMATL.EQ.12.)GOTO 60
C
C     Calculate cost of five major Wetox components.
C
      COSTTIT=1714.*((WTMET+TUBEWT*1)**(-.38))*(WTMET+TUBEWT*1)*RN
      COSTREA=STEEL+COSTTIT
      COSTAG=.2*CN*COSTREA
      GOTO 70
   50 COSTTIT=2255.*((WTMET+TUBEWT*1)**(-.38))*(WTMET+TUBEWT*1)*RN
      COSTREA=STEEL+COSTTIT
      COSTAG=.18*CN*COSTREA
      GOTO 70
   60 COSTTIT=1804.*((WTMET+TUBEWT*1)**(-.38))*(WTMET+TUBEWT*1)*RN
      COSTREA=STEEL+COSTTIT
      COSTAG=.2*CN*COSTREA
   70 CONTINUE
      COSTCOM=EXP(.768*ALOG(COMPHP)+7.44)*1.35
      COSTHE=.10*COSTREA
      IF(OPT.EQ.3.)COSTHE=.30*COSTREA
      IF(OPT.EQ.6.)COSTHE=.30*COSTREA
      IF(OPT.EQ.1.)COSTHE=.15*COSTREA
      IF(OPT.EQ.4.)COSTHE=.15*COSTREA
      COSTPUM=89.*(REACP+.1)*FEEDRAT
      COSTMAJ=COSTREA+COSTAG+COSTCOM+COSTHE+COSTPUM
C
C     Calculate 'other' plant capital costs based on major equipment.
C
      COSTIN=.25*COSTMAJ
      COSTPIP=.12*COSTMAJ
      COSTINS=.03*COSTMAJ
      COSTCON=.13*COSTMAJ
      COSTEL=.1*COSTMAJ
      CONTIN=.25*COSTMAJ
      COSTETC=.07*COSTMAJ
      TOTCOST=COSTMAJ*2.
      OPO2=0.
      COSTO2=0.
      IF(OXIDF.EQ..2314)GOTO 80
C
C     Calculate cost of oxygen plant if oxygen system selected.
C
      COSTO2=10950000.*(QOXY/316.)**.6


      ENO2=173125.*QOXY
      ENCOST=ENO2*CKWHR
      OPO2=1.65*ENCOST
   80 CONTINUE
C
C     Calculate system annual operating costs.
C
      OPLAB=438000.
      OPF=CF*FUEL*FEEDRAT*475.
      OPEL=COMPKW*8712.*CKWHR
      OPM=.04*TOTCOST
      OPC=FUEL*100.*FEEDRAT*(.75*ALIME+ANAOH*.1)
      OPW=4000.*FUEL*FEEDRAT
      CO2V=0.
      IF(OPT.EQ.6.)CO2V=CO2P*CO2*330.
      ANNOP=OPO2+OPLAB+OPF+OPEL+OPM+OPC+OPW+CCH4-CVAL-CO2V
C
C     Calculate total and annual capital costs.
C
      TOTCAP=COSTO2+TOTCOST
      ANNCAP=(COSTO2+TOTCOST)*CRF
C
C     Summarize total annual costs, and calculate steam costs ($/GJ).
```

```
C
  300 CONTINUE
  200 CONTINUE
  100 CONTINUE
      STOP
      END
```

```
*C
       ANNTOT=ANNOP+ANNCAP
       HWCOST=0.
       STCOST=0.
       VPEOUT=0.
       FEED=FEEDRAT/RN
       IF(OPT.EQ.3.)GOTO 798
       IF(OPT.EQ.6.)GOTO 798
       VPEOUT=HEATOUT-HLPEHR
       IF(HEXC.GT.0.)VPEOUT=HEATOUT-HEXCT-HLPEHR
       STCOST=ANNTOT/VPEOUT/7.92
       IF(STCOST.GT.STM)GOTO 290
       GOTO 799
   798 CONTINUE
       HWCOST=ANNTOT/HEATOUT/7.92
       IF(HWCOST.GT.STM)GOTO 290
   799 CONTINUE
 C
 C     Write and format desired output results.
 C
       WRITE(*,800)TCR,REACP,VPFR,FUEL
   800 FORMAT(////,3X,'T='F4.0,5X,'P='F4.1,5X,'V/F='F4.3,5X,'FC='F4.3,/
       WRITE(*,805)RN,VOLRT,FEED


   805 FORMAT(3X,F3.1,2X,'UNITS AT 'F5.2,' m3 EACH',5X,'FEED L/M='F6.1)
       WRITE(*,810)DIA,ENGTH,TDIA,TUBEL
   810 FORMAT(3X,'VESS='F5.2,' BY'F6.2,8X,'#1TUBE='F4.2,' BY',F6.0)
       IF(TUBEL.GT.COILL)WRITE(*,305)COILL
   305 FORMAT(3X,'PRACTICAL COIL LENGTH IS ONLY 'F6.0,' m')
       WRITE(*,811)TOTTVOL,CWFL
   811 FORMAT(3X,'COIL VOL(m3)='F5.2,9X,'CW FLOW(L/M)='F6.1,'  PER UNIT

       WRITE(*,815)HEXCT,VPEOUT
   815 FORMAT(3X,'COILS(MJ/H)='F8.0,7X,'VPE ST(MJ/H)='F8.0)
       WRITE(*,812)HLPEHR,COSTO2
   812 FORMAT(3X,'LPE(MJ/H)='F8.0,9X,'O2 PLANT($)='F9.0)
       WRITE(*,820)ANNOP,ANNCAP,TOTCAP
   820 FORMAT(3X,'OP $/Y='F9.0,11X,'CAP $/Y='F9.0,9X,'TOT CAP $='F9.0)
       WRITE(*,825)HWCOST,STCOST
   825 FORMAT(3X,'HOT WATER $/GJ='F5.2,7X,'VPE ST $/GJ='F6.2)
   290 CONTINUE
 C
 C     Increment reactor pressure.
 C
       IF(OXIDF.EQ..2314)REACP=REACP+.7
       IF(OXIDF.EQ.1.)REACP=REACP+1.8
 C
 C     Terminate three system do loops.
```

APPENDIX I

Options 1 - 6, Base Case
Results Printouts

OPTION 1

Base Case Results

```
WETOX HEAT OUTPUT(MJ/H)= 264000.          OPTION 1.

    O2 CONC= .2314       #COMP=6.       TIT GR= 12.

          .2314      452160.0000       17927.0000          1.9900          .9000
         6.0000      264000.0000            .9500         12.0000         4.5000
         1.0000
          .0300          41.2000          45.0000        300.0000          .1600
          .0024           6.8000           3.5000          3.5000          .0300
         1.0000            .3000


  T=290.      P=14.8      V/F=.900      FC=.132

  1.0  UNITS AT 13.14 m3 EACH      FEED L/M=1119.3
  VESS= 1.40 BY  8.41           #1TUBE=4.18 BY  302.
  PRACTICAL COIL LENGTH IS ONLY   239. m
  COIL VOL(m3)= 1.52            CW FLOW(L/M)= 695.5  PER UNIT
  COILS(MJ/H)= 104322.          VPE ST(MJ/H)= 151108.
  LPE(MJ/H)=   8570.            O2 PLANT($)=          0.
  OP $/Y= 5855486.              CAP $/Y= 2053744.       TOT CAP $=12835900.
  HOT WATER $/GJ=  .00          VPE ST $/GJ=  6.61



  T=300.      P=15.9      V/F=.700      FC=.089

  2.0  UNITS AT 23.22 m3 EACH      FEED L/M= 830.6
  VESS= 1.69 BY 10.15           #1TUBE=2.08 BY  295.
  COIL VOL(m3)=  .46            CW FLOW(L/M)= 167.0  PER UNIT
  COILS(MJ/H)=  50109.          VPE ST(MJ/H)= 174422.
  LPE(MJ/H)=  39469.            O2 PLANT($)=          0.
  OP $/Y= 6707129.              CAP $/Y= 2631061.       TOT CAP $=16444130.
  HOT WATER $/GJ=  .00          VPE ST $/GJ=  6.76
```

6

```
T=300.     P=15.9     V/F=.800     FC=.102

2.0  UNITS AT 13.54 m3 EACH      FEED L/M= 726.8
VESS= 1.42 BY  8.50         #1TUBE=2.40 BY  341.
COIL VOL(m3)=  .66          CW FLOW(L/M)= 221.8  PER UNIT
COILS(MJ/H)=  66555.        VPE ST(MJ/H)= 174422.
LPE(MJ/H)=  23024.          O2 PLANT($)=         0.
OP $/Y= 6663347.            CAP $/Y= 2455931.         TOT CAP $=15349570.
HOT WATER $/GJ=  .00        VPE ST $/GJ=  6.60

T=300.     P=15.9     V/F=.900     FC=.114

1.0  UNITS AT 12.04 m3 EACH      FEED L/M=1292.0
VESS= 1.36 BY  8.17         #1TUBE=3.70 BY  263.
PRACTICAL COIL LENGTH IS ONLY   248. m
COIL VOL(m3)= 1.04          CW FLOW(L/M)= 529.0  PER UNIT
COILS(MJ/H)=  79346.        VPE ST(MJ/H)= 174422.
LPE(MJ/H)=  10233.          O2 PLANT($)=         0.
OP $/Y= 6594232.            CAP $/Y= 2179472.         TOT CAP $=13621700.
HOT WATER $/GJ=  .00        VPE ST $/GJ=  6.35


T=300.     P=16.6     V/F=.900     FC=.125

1.0  UNITS AT 10.99 m3 EACH      FEED L/M=1179.6
VESS= 1.32 BY  7.93         #1TUBE=4.06 BY  288.
PRACTICAL COIL LENGTH IS ONLY   217. m
COIL VOL(m3)= 1.34          CW FLOW(L/M)= 636.1  PER UNIT
COILS(MJ/H)=  95409.        VPE ST(MJ/H)= 159248.
LPE(MJ/H)=   9343.          O2 PLANT($)=         0.
OP $/Y= 6203490.            CAP $/Y= 2157698.         TOT CAP $=13485610.
HOT WATER $/GJ=  .00        VPE ST $/GJ=  6.63
```

```
T=310.     P=17.2     V/F=.700     FC=.078

2.0  UNITS AT 21.58 m3 EACH      FEED L/M= 954.0
VESS= 1.65 BY  9.91          #1TUBE=1.23 BY  172.
COIL VOL(m3)=  .12           CW FLOW(L/M)=  56.0  PER UNIT
COILS(MJ/H)=  16811.         VPE ST(MJ/H)= 200343.
LPE(MJ/H)=  46846.           O2 PLANT($)=       0.
OP $/Y= 7533590.             CAP $/Y= 2808859.       TOT CAP $=17555370.
HOT WATER $/GJ=  .00         VPE ST $/GJ=  6.52


T=310.     P=17.2     V/F=.800     FC=.089

2.0  UNITS AT 12.59 m3 EACH      FEED L/M= 834.8
VESS= 1.38 BY  8.29          #1TUBE=1.80 BY  252.
COIL VOL(m3)=  .30           CW FLOW(L/M)= 121.1  PER UNIT
COILS(MJ/H)=  36330.         VPE ST(MJ/H)= 200343.
LPE(MJ/H)=  27327.           O2 PLANT($)=       0.
OP $/Y= 7485207.             CAP $/Y= 2615323.       TOT CAP $=16345770.
HOT WATER $/GJ=  .00         VPE ST $/GJ=  6.37


T=310.     P=17.2     V/F=.900     FC=.100

1.0  UNITS AT 11.19 m3 EACH      FEED L/M=1484.0
VESS= 1.33 BY  7.98          #1TUBE=3.04 BY  212.
COIL VOL(m3)=  .58           CW FLOW(L/M)= 343.4  PER UNIT
COILS(MJ/H)=  51512.         VPE ST(MJ/H)= 200343.
LPE(MJ/H)=  12145.           O2 PLANT($)=       0.
OP $/Y= 7414514.             CAP $/Y= 2332552.       TOT CAP $=14578450.
HOT WATER $/GJ=  .00         VPE ST $/GJ=  6.14
Stop - Program terminated.
```

OPTION 2

Base Case Results

```
WETOX HEAT OUTPUT(MJ/H)= 264000.          OPTION 2.

     O2 CONC= .2314       #COMP=6.       TIT GR= 12.

          .2314     452160.0000     17927.0000
         6.0000     264000.0000                     1.9900            .9000
         1.0000                          .9500     12.0000           4.5000
          .0300
          .0024         41.2000
         2.0000          6.8000        45.0000     300.0000            .1600
                          .3000         3.5000       3.5000            .0300


  T=290.      P=14.8      V/F=.900      FC=.132

  1.0  UNITS AT 13.14 m3 EACH       FEED L/M=1119.3
  VESS= 1.40 BY  8.41           #1TUBE=4.18 BY  302.
  PRACTICAL COIL LENGTH IS ONLY   239. m
  COIL VOL(m3)= 1.52            CW FLOW(L/M)= 695.5  PER UNIT
  COILS(MJ/H)= 104322.          VPE ST(MJ/H)= 151108.
  LPE(MJ/H)=   8570.            O2 PLANT($)=        0.
  OP $/Y= 5854492.              CAP $/Y= 2049767.         TOT CAP $=12811050.
  HOT WATER $/GJ=  .00          VPE ST $/GJ=  6.60


  T=300.      P=15.9      V/F=.700      FC=.089

  2.0  UNITS AT 23.22 m3 EACH       FEED L/M= 830.6
  VESS= 1.69 BY 10.15           #1TUBE=2.08 BY  295.
  COIL VOL(m3)=  .46            CW FLOW(L/M)= 167.0  PER UNIT
  COILS(MJ/H)=  50109.          VPE ST(MJ/H)= 174422.
  LPE(MJ/H)=  39469.            O2 PLANT($)=        0.
  OP $/Y= 6704672.              CAP $/Y= 2621232.         TOT CAP $=16382700.
  HOT WATER $/GJ=  .00          VPE ST $/GJ=  6.75
```

```
T=300.      P=15.9      V/F=.800      FC=.102

2.0  UNITS AT 13.54 m3 EACH      FEED L/M= 726.8
VESS= 1.42 BY  8.50         #1TUBE=2.40 BY  341.
COIL VOL(m3)=  .66          CW FLOW(L/M)= 221.8  PER UNIT
COILS(MJ/H)=  66555.        VPE ST(MJ/H)= 174422.
LPE(MJ/H)=  23024.          O2 PLANT($)=        0.
OP $/Y= 6661316.            CAP $/Y= 2447810.        TOT CAP $=15298810.
HOT WATER $/GJ=  .00        VPE ST $/GJ=  6.59

T=300.      P=15.9      V/F=.900      FC=.114

1.0  UNITS AT 12.04 m3 EACH      FEED L/M=1292.0
VESS= 1.36 BY  8.17         #1TUBE=3.70 BY  263.
PRACTICAL COIL LENGTH IS ONLY   248. m
COIL VOL(m3)= 1.04          CW FLOW(L/M)= 529.0  PER UNIT
COILS(MJ/H)=  79346.        VPE ST(MJ/H)= 174422.
LPE(MJ/H)=  10233.          O2 PLANT($)=        0.
OP $/Y= 6593280.            CAP $/Y= 2175663.        TOT CAP $=13597890.
HOT WATER $/GJ=  .00        VPE ST $/GJ=  6.35


T=300.      P=16.6      V/F=.900      FC=.125

1.0  UNITS AT 10.99 m3 EACH      FEED L/M=1179.6
VESS= 1.32 BY  7.93         #1TUBE=4.06 BY  288.
PRACTICAL COIL LENGTH IS ONLY   217. m
COIL VOL(m3)= 1.34          CW FLOW(L/M)= 636.1  PER UNIT
COILS(MJ/H)=  95409.        VPE ST(MJ/H)= 159248.
LPE(MJ/H)=   9343.          O2 PLANT($)=        0.
OP $/Y= 6202560.            CAP $/Y= 2153982.        TOT CAP $=13462390.
HOT WATER $/GJ=  .00        VPE ST $/GJ=  6.63
```

```
T=310.      P=17.2      V/F=.700      FC=.078

2.0  UNITS AT 21.58 m3 EACH      FEED L/M= 954.0
VESS= 1.65 BY   9.91          #1TUBE=1.23 BY  172.
COIL VOL(m3)=   .12           CW FLOW(L/M)=   56.0  PER UNIT
COILS(MJ/H)=   16811.         VPE ST(MJ/H)= 200343.
LPE(MJ/H)=  46846.            O2 PLANT($)=          0.
OP $/Y= 7531256.              CAP $/Y= 2799522.          TOT CAP $=17497010.
HOT WATER $/GJ=   .00         VPE ST $/GJ=   6.51


T=310.      P=17.2      V/F=.800      FC=.089

2.0  UNITS AT 12.59 m3 EACH      FEED L/M= 834.8
VESS= 1.38 BY   8.29          #1TUBE=1.80 BY  252.
COIL VOL(m3)=   .30           CW FLOW(L/M)= 121.1  PER UNIT
COILS(MJ/H)=   36330.         VPE ST(MJ/H)= 200343.
LPE(MJ/H)=  27327.            O2 PLANT($)=          0.
OP $/Y= 7483276.              CAP $/Y= 2607601.          TOT CAP $=16297510.
HOT WATER $/GJ=   .00         VPE ST $/GJ=   6.36


T=310.      P=17.2      V/F=.900      FC=.100

1.0  UNITS AT 11.19 m3 EACH      FEED L/M=1484.0
VESS= 1.33 BY   7.98          #1TUBE=3.04 BY  212.
COIL VOL(m3)=   .58           CW FLOW(L/M)= 343.4  PER UNIT
COILS(MJ/H)=   51512.         VPE ST(MJ/H)= 200343.
LPE(MJ/H)=  12145.            O2 PLANT($)=          0.
OP $/Y= 7413601.              CAP $/Y= 2328900.          TOT CAP $=14555620.
HOT WATER $/GJ=   .00         VPE ST $/GJ=   6.14
Stop - Program terminated.

B>
```

OPTION 3

Base Case Results

```
   O2 CONC= .2314       #COMP=6.       TIT GR= 12.

      .2314     452160.0000      17927.0000          1.9900          .9000
     6.0000     264000.0000           .9500         12.0000         4.5000
     1.0000
      .0300         41.2000         45.0000        300.0000          .1600
      .0024          5.2000          3.5000          3.5000          .0300
     3.0000           .3000


T=260.     P=12.0     V/F=.900     FC=.210
                        F=.900     FC=.210

1.0  UNITS AT 18.50 m3 EACH      FEED L/M= 704.7
VESS= 1.57 BY  9.42         #1TUBE=5.08 BY  385.
PRACTICAL COIL LENGTH IS ONLY   255. m
COIL VOL(m3)= 2.93          CW FLOW(L/M)=1093.5  PER UNIT
COILS(MJ/H)= 164032.        VPE ST(MJ/H)=       0.
LPE(MJ/H)=   4837.          O2 PLANT($)=        0.
OP $/Y= 8759570.            CAP $/Y= 1815855.        TOT CAP $=11349090.
HOT WATER $/GJ= 5.06        VPE ST $/GJ=   .00


T=260.     P=12.7     V/F=.900     FC=.230

1.0  UNITS AT 16.89 m3 EACH      FEED L/M= 643.4
VESS= 1.52 BY  9.14         #1TUBE=5.21 BY  396.
PRACTICAL COIL LENGTH IS ONLY   235. m
COIL VOL(m3)= 3.15          CW FLOW(L/M)=1151.5  PER UNIT
COILS(MJ/H)= 172728.        VPE ST(MJ/H)=       0.
LPE(MJ/H)=   4416.          O2 PLANT($)=        0.
OP $/Y= 8804244.            CAP $/Y= 1814493.        TOT CAP $=11340580.
HOT WATER $/GJ= 5.08        VPE ST $/GJ=   .00
```

```
T=270.     P=13.5     V/F=.900     FC=.196

1.0  UNITS AT 14.89 m3 EACH      FEED L/M= 755.0
VESS= 1.46 BY  8.77           #1TUBE=5.01 BY  373.
PRACTICAL COIL LENGTH IS ONLY   224. m
COIL VOL(m3)= 2.72            CW FLOW(L/M)=1044.7  PER UNIT
COILS(MJ/H)= 156700.          VPE ST(MJ/H)=        0.
LPE(MJ/H)=   5381.            O2 PLANT($)=         0.
OP $/Y= 8869410.              CAP $/Y= 1876630.         TOT CAP $=11728940.
HOT WATER $/GJ= 5.14          VPE ST $/GJ=    .00

T=270.     P=14.2     V/F=.900     FC=.213

1.0  UNITS AT 13.69 m3 EACH      FEED L/M= 694.5
VESS= 1.42 BY  8.53           #1TUBE=5.14 BY  384.
PRACTICAL COIL LENGTH IS ONLY   207. m
COIL VOL(m3)= 2.93            CW FLOW(L/M)=1101.9  PER UNIT
COILS(MJ/H)= 165287.          VPE ST(MJ/H)=        0.
LPE(MJ/H)=   4951.            O2 PLANT($)=         0.
OP $/Y= 8909359.              CAP $/Y= 1873777.         TOT CAP $=11711100.
HOT WATER $/GJ= 5.16          VPE ST $/GJ=    .00


T=270.     P=14.9     V/F=.900     FC=.230

1.0  UNITS AT 12.68 m3 EACH      FEED L/M= 643.1
VESS= 1.39 BY  8.31           #1TUBE=5.26 BY  392.
PRACTICAL COIL LENGTH IS ONLY   193. m
COIL VOL(m3)= 3.11            CW FLOW(L/M)=1150.7  PER UNIT
COILS(MJ/H)= 172602.          VPE ST(MJ/H)=        0.
LPE(MJ/H)=   4584.            O2 PLANT($)=         0.
OP $/Y= 8947943.              CAP $/Y= 1872381.         TOT CAP $=11702380.
HOT WATER $/GJ= 5.18          VPE ST $/GJ=    .00
```

```
T=260.      P=13.4      V/F=.900      FC=.250

1.0  UNITS AT 15.54 m3 EACH      FEED L/M= 591.9
VESS= 1.48 BY  8.89          #1TUBE=5.32 BY  404.
PRACTICAL COIL LENGTH IS ONLY   219. m
COIL VOL(m3)= 3.33           CW FLOW(L/M)=1200.2  PER UNIT
COILS(MJ/H)= 180033.         VPE ST(MJ/H)=        0.
LPE(MJ/H)=   4063.           O2 PLANT($)=         0.
OP $/Y= 8847147.             CAP $/Y= 1814557.        TOT CAP $=11340980.
HOT WATER $/GJ= 5.10         VPE ST $/GJ=    .00

T=260.      P=14.1      V/F=.900      FC=.270

1.0  UNITS AT 14.39 m3 EACH      FEED L/M= 548.0
VESS= 1.44 BY  8.67          #1TUBE=5.42 BY  411.
PRACTICAL COIL LENGTH IS ONLY   205. m
COIL VOL(m3)= 3.50           CW FLOW(L/M)=1241.7  PER UNIT
COILS(MJ/H)= 186255.         VPE ST(MJ/H)=        0.
LPE(MJ/H)=   3762.           O2 PLANT($)=         0.
OP $/Y= 8888383.             CAP $/Y= 1815673.        TOT CAP $=11347950.
HOT WATER $/GJ= 5.12         VPE ST $/GJ=    .00

T=260.      P=14.8      V/F=.900      FC=.290

1.0  UNITS AT 13.40 m3 EACH      FEED L/M= 510.2
VESS= 1.41 BY  8.47          #1TUBE=5.49 BY  417.
PRACTICAL COIL LENGTH IS ONLY   193. m
COIL VOL(m3)= 3.64           CW FLOW(L/M)=1277.5  PER UNIT
COILS(MJ/H)= 191618.         VPE ST(MJ/H)=        0.
LPE(MJ/H)=   3502.           O2 PLANT($)=         0.
OP $/Y= 8928061.             CAP $/Y= 1817581.        TOT CAP $=11359880.
HOT WATER $/GJ= 5.14         VPE ST $/GJ=    .00
```

```
T=270.     P=12.8     V/F=.900     FC=.179

1.0  UNITS AT 16.30 m3 EACH      FEED L/M= 826.9
VESS= 1.51 BY  9.03          #1TUBE=4.84 BY  361.
PRACTICAL COIL LENGTH IS ONLY   244. m
COIL VOL(m3)= 2.47           CW FLOW(L/M)= 976.5  PER UNIT
COILS(MJ/H)= 146476.         VPE ST(MJ/H)=        0.
LPE(MJ/H)=   5894.           O2 PLANT($)=         0.
OP $/Y= 8828043.             CAP $/Y= 1881416.         TOT CAP $=11758850.
HOT WATER $/GJ= 5.12         VPE ST $/GJ=    .00
```

OPTION 4

Base Case Results

```
WETOX HEAT OUTPUT(MJ/H)= 264000.          OPTION 4.

    O2 CONC=1.0000       #COMP=6.       TIT GR= 12.

        1.0000      452160.0000       17927.0000            1.9900             .9000
        6.0000      264000.0000            .9500           12.0000            4.5000
        1.0000
         .0300          41.2000          45.0000          300.0000             .1600
         .0024           9.5000           3.5000            3.5000             .0300
        4.0000            .3000


  T=320.      P=14.8      V/F=.500      FC=.100

  2.0  UNITS AT 23.08 m3 EACH      FEED L/M= 741.7
  VESS= 1.69 BY 10.13          #1TUBE=2.90 BY  399.
  COIL VOL(m3)=   .97          CW FLOW(L/M)= 300.3  PER UNIT
  COILS(MJ/H)=  90094.         VPE ST(MJ/H)= 111250.
  LPE(MJ/H)=  62656.           O2 PLANT($)=12031240.
  OP $/Y= 4873102.             CAP $/Y= 3415572.       TOT CAP $=21347330.
  HOT WATER $/GJ=  .00         VPE ST $/GJ=  9.41


  T=320.      P=14.8      V/F=.500      FC=.100

  2.0  UNITS AT 23.08 m3 EACH      FEED L/M= 741.7
  VESS= 1.69 BY 10.13          #1TUBE=2.90 BY  399.
  COIL VOL(m3)=   .97          CW FLOW(L/M)= 300.3  PER UNIT
  COILS(MJ/H)=  90094.         VPE ST(MJ/H)= 111250.
  LPE(MJ/H)=  62656.           O2 PLANT($)=12031240.
  OP $/Y= 4873102.             CAP $/Y= 3415572.       TOT CAP $=21347330.
  HOT WATER $/GJ=  .00         VPE ST $/GJ=  9.41
```

```
T=320.     P=14.8     V/F=.600     FC=.120

2.0  UNITS AT 15.39 m3 EACH      FEED L/M= 618.1
VESS= 1.48 BY  8.86          #1TUBE=3.22 BY  443.
PRACTICAL COIL LENGTH IS ONLY    325. m
COIL VOL(m3)= 1.28             CW FLOW(L/M)= 369.9  PER UNIT
COILS(MJ/H)= 110979.           VPE ST(MJ/H)= 111250.
LPE(MJ/H)=  41771.             O2 PLANT($)=12031240.
OP $/Y= 4831716.               CAP $/Y= 3250031.          TOT CAP $=20312690.
HOT WATER $/GJ=  .00           VPE ST $/GJ=  9.17

T=320.     P=14.8     V/F=.700     FC=.140

1.0  UNITS AT 19.78 m3 EACH      FEED L/M=1059.5
VESS= 1.60 BY  9.63          #1TUBE=4.85 BY  334.
PRACTICAL COIL LENGTH IS ONLY    277. m
COIL VOL(m3)= 1.97             CW FLOW(L/M)= 839.3  PER UNIT
COILS(MJ/H)= 125897.           VPE ST(MJ/H)= 111250.
LPE(MJ/H)=  26853.             O2 PLANT($)=12031240.
OP $/Y= 4765979.               CAP $/Y= 2987081.          TOT CAP $=18669250.
HOT WATER $/GJ=  .00           VPE ST $/GJ=  8.80
```

```
T=320.     P=14.8     V/F=.800     FC=.160

 1.0  UNITS AT 11.54 m3 EACH     FEED L/M= 927.1
 VESS= 1.34 BY  8.06          #1TUBE=5.06 BY  348.
 PRACTICAL COIL LENGTH IS ONLY   187. m
 COIL VOL(m3)= 2.21           CW FLOW(L/M)= 913.9  PER UNIT
 COILS(MJ/H)= 137086.         VPE ST(MJ/H)= 111250.
 LPE(MJ/H)=  15664.           O2 PLANT($)=12031240.
 OP $/Y= 4742322.             CAP $/Y= 2892449.        TOT CAP $=18077810.
 HOT WATER $/GJ=  .00         VPE ST $/GJ=  8.67


 T=320.     P=14.8     V/F=.900     FC=.179

 1.0  UNITS AT  5.13 m3 EACH     FEED L/M= 824.1
 VESS= 1.03 BY  6.17          #1TUBE=5.22 BY  359.
 PRACTICAL COIL LENGTH IS ONLY   107. m
 COIL VOL(m3)= 2.41           CW FLOW(L/M)= 971.9  PER UNIT
 COILS(MJ/H)= 145788.         VPE ST(MJ/H)= 111250.
 LPE(MJ/H)=   6962.           O2 PLANT($)=12031240.
 OP $/Y= 4720752.             CAP $/Y= 2806170.        TOT CAP $=17538560.
 HOT WATER $/GJ=  .00         VPE ST $/GJ=  8.54
Stop - Program terminated.
```

OPTION 5

Base Case Results

```
WETOX HEAT OUTPUT(MJ/H)= 264000.          OPTION 5.

     O2 CONC=1.0000       #COMP=6.        TIT GR= 12.

       1.0000      452160.0000     17913.0000           1.9900           .9000
       6.0000      264000.0000          .9500          12.0000          4.5000
       1.0000
        .0300          41.2000        45.0000         300.0000           .1600
        .0024           9.5000         3.5000           3.5000           .0300
       5.0000            .3000


T=320.      P=14.8      V/F=.500      FC=.100

 2.0  UNITS AT 22.89 m3 EACH      FEED L/M= 741.7
 VESS= 1.68 BY 10.10           #1TUBE=2.90 BY  400.
 COIL VOL(m3)=  .97            CW FLOW(L/M)= 300.3  PER UNIT
 COILS(MJ/H)=  90094.          VPE ST(MJ/H)= 111250.
 LPE(MJ/H)=  62656.            O2 PLANT($)=12031240.
 OP $/Y= 4870256.              CAP $/Y= 3404188.         TOT CAP $=21276180.
 HOT WATER $/GJ=  .00          VPE ST $/GJ=  9.39

T=320.      P=14.8      V/F=.600      FC=.120

 2.0  UNITS AT 15.26 m3 EACH      FEED L/M= 618.1
 VESS= 1.47 BY  8.84           #1TUBE=3.22 BY  444.
 PRACTICAL COIL LENGTH IS ONLY   323. m
 COIL VOL(m3)= 1.28
 COILS(MJ/H)= 110979.          CW FLOW(L/M)= 369.9  PER UNIT
 LPE(MJ/H)=  41771.            VPE ST(MJ/H)= 111250.
 OP $/Y= 4829254.              O2 PLANT($)=12031240.
 HOT WATER $/GJ=  .00          CAP $/Y= 3240180.         TOT CAP $=20251130.
                               VPE ST $/GJ=  9.16
```

```
T=320.      P=14.8      V/F=.700      FC=.140

1.0  UNITS AT 19.62 m3 EACH       FEED L/M=1059.5
VESS= 1.60 BY  9.60           #1TUBE=4.86 BY  334.
PRACTICAL COIL LENGTH IS ONLY   275. m
COIL VOL(m3)= 1.97            CW FLOW(L/M)= 839.3  PER UNIT
COILS(MJ/H)= 125897.          VPE ST(MJ/H)= 111250.
LPE(MJ/H)=  26853.            O2 PLANT($)=12031240.
OP $/Y= 4764651.              CAP $/Y= 2981768.        TOT CAP $=18636056.
HOT WATER $/GJ=  .00          VPE ST $/GJ=  8.79

T=320.      P=14.8      V/F=.800      FC=.160

1.0  UNITS AT 11.44 m3 EACH       FEED L/M= 927.1
VESS= 1.34 BY  8.04           #1TUBE=5.07 BY  349.
PRACTICAL COIL LENGTH IS ONLY   186. m
COIL VOL(m3)= 2.21            CW FLOW(L/M)= 913.9  PER UNIT
COILS(MJ/H)= 137086.          VPE ST(MJ/H)= 111250.
LPE(MJ/H)=  15664.            O2 PLANT($)=12031240.
OP $/Y= 4741234.              CAP $/Y= 2888100.        TOT CAP $=18050620.
HOT WATER $/GJ=  .00          VPE ST $/GJ=  8.66


T=320.      P=14.8      V/F=.900      FC=.179

1.0  UNITS AT  5.09 m3 EACH       FEED L/M= 824.1
VESS= 1.02 BY  6.15           #1TUBE=5.23 BY  360.
PRACTICAL COIL LENGTH IS ONLY   106. m
COIL VOL(m3)= 2.41            CW FLOW(L/M)= 971.9  PER UNIT
COILS(MJ/H)= 145788.          VPE ST(MJ/H)= 111250.
LPE(MJ/H)=   6962.            O2 PLANT($)=12031240.
OP $/Y= 4719932.              CAP $/Y= 2802892.        TOT CAP $=17518070.
HOT WATER $/GJ=  .00          VPE ST $/GJ=  8.54
```

OPTION 6

Base Case Results

```
WETOX HEAT OUTPUT(MJ/H)= 264000.          OPTION 6.

    O2 CONC=1.0000        #COMP=6.      TIT GR= 12.

          1.0000     452160.0000      17913.0000          1.9900          .9000
          6.0000     264000.0000           .9500         12.0000         4.5000
          1.0000
           .0300         41.2000         45.0000        300.0000          .1600
           .0024          2.9000          3.5000          3.5000          .0300
          6.0000           .3000


 T=260.     P= 6.4     V/F=.900     FC=.210

 1.0  UNITS AT 18.28 m3 EACH      FEED L/M= 704.7
 VESS= 1.56 BY  9.38          #1TUBE=5.08 BY  386.
 PRACTICAL COIL LENGTH IS ONLY   253. m
 COIL VOL(m3)= 2.93           CW FLOW(L/M)=1093.5  PER UNIT
 COILS(MJ/H)= 164032.         VPE ST(MJ/H)=        0.
 LPE(MJ/H)=    4837.          O2 PLANT($)=12031240.
 OP $/Y= 3201998.             CAP $/Y= 2634817.        TOT CAP $=16467600.
 HOT WATER $/GJ= 2.79         VPE ST $/GJ=    .00

 T=270.     P= 7.2     V/F=.900     FC=.179

 1.0  UNITS AT 16.11 m3 EACH      FEED L/M= 826.9
 VESS= 1.50 BY  9.00          #1TUBE=4.84 BY  361.
 PRACTICAL COIL LENGTH IS ONLY   242. m
 COIL VOL(m3)= 2.47           CW FLOW(L/M)= 976.5  PER UNIT
 COILS(MJ/H)= 146476.         VPE ST(MJ/H)=        0.
 LPE(MJ/H)=    5894.          O2 PLANT($)=12031240.
 OP $/Y= 3193334.             CAP $/Y= 2658927.        TOT CAP $=16618290.
 HOT WATER $/GJ= 2.80         VPE ST $/GJ=    .00
```

```
T=280.      P= 9.9      V/F=.800      FC=.281

1.0  UNITS AT 15.71 m3 EACH       FEED L/M= 527.1
VESS= 1.49 BY  8.92          #1TUBE=5.62 BY  412.
PRACTICAL COIL LENGTH IS ONLY   210. m
COIL VOL(m3)= 3.61            CW FLOW(L/M)=1286.3  PER UNIT
COILS(MJ/H)= 192951.          VPE ST(MJ/H)=        0.
LPE(MJ/H)=    7793.           O2 PLANT($)=12031240.
OP $/Y= 3240726.              CAP $/Y= 2660183.         TOT CAP $=16626140.
HOT WATER $/GJ= 2.82          VPE ST $/GJ=    .00

T=280.      P= 8.1      V/F=.900      FC=.153

1.0  UNITS AT 14.38 m3 EACH       FEED L/M= 964.7
VESS= 1.44 BY  8.67          #1TUBE=4.55 BY  334.
PRACTICAL COIL LENGTH IS ONLY   236. m
COIL VOL(m3)= 2.01            CW FLOW(L/M)= 844.2  PER UNIT
COILS(MJ/H)= 126635.          VPE ST(MJ/H)=        0.
LPE(MJ/H)=    7131.           O2 PLANT($)=12031240.
OP $/Y= 3223647.              CAP $/Y= 2710688.         TOT CAP $=16941800.
HOT WATER $/GJ= 2.84          VPE ST $/GJ=    .00


T=290.      P=10.9      V/F=.800      FC=.242

1.0  UNITS AT 14.21 m3 EACH       FEED L/M= 611.6
VESS= 1.44 BY  8.63          #1TUBE=5.51 BY  398.
PRACTICAL COIL LENGTH IS ONLY   200. m
COIL VOL(m3)= 3.28            CW FLOW(L/M)=1208.3  PER UNIT
COILS(MJ/H)= 181239.          VPE ST(MJ/H)=        0.
LPE(MJ/H)=    9365.           O2 PLANT($)=12031240.
OP $/Y= 3265748.              CAP $/Y= 2700517.         TOT CAP $=16878230.
HOT WATER $/GJ= 2.85          VPE ST $/GJ=    .00
```

```
T=290.      P= 9.1      V/F=.900      FC=.132

1.0  UNITS AT 13.00 m3 EACH      FEED L/M=1119.3
VESS= 1.40 BY  8.38          #1TUBE=4.18 BY  302.
PRACTICAL COIL LENGTH IS ONLY   237. m
COIL VOL(m3)= 1.52          CW FLOW(L/M)= 695.5  PER UNIT
COILS(MJ/H)= 104322.        VPE ST(MJ/H)=      0.
LPE(MJ/H)=   8570.          O2 PLANT($)=12031240.
OP $/Y= 3258226.            CAP $/Y= 2778606.        TOT CAP $=17366290.
HOT WATER $/GJ= 2.89        VPE ST $/GJ=   .00


T=290.      P=10.9      V/F=.900      FC=.272

1.0  UNITS AT  6.31 m3 EACH      FEED L/M= 543.7
VESS= 1.10 BY  6.61          #1TUBE=5.59 BY  404.
PRACTICAL COIL LENGTH IS ONLY   116. m
COIL VOL(m3)= 3.42          CW FLOW(L/M)=1242.9  PER UNIT
COILS(MJ/H)= 186442.        VPE ST(MJ/H)=      0.
LPE(MJ/H)=   4162.          O2 PLANT($)=12031240.
OP $/Y= 3248193.            CAP $/Y= 2630296.        TOT CAP $=16439350.
HOT WATER $/GJ= 2.81        VPE ST $/GJ=   .00

T=300.      P=13.9      V/F=.700      FC=.278

1.0  UNITS AT 14.75 m3 EACH      FEED L/M= 532.8
VESS= 1.46 BY  8.74          #1TUBE=5.82 BY  413.
PRACTICAL COIL LENGTH IS ONLY   196. m
COIL VOL(m3)= 3.64          CW FLOW(L/M)=1302.6  PER UNIT
COILS(MJ/H)= 195394.        VPE ST(MJ/H)=      0.
LPE(MJ/H)=  12660.          O2 PLANT($)=12031240.
OP $/Y= 3312683.            CAP $/Y= 2740769.        TOT CAP $=17129810.
HOT WATER $/GJ= 2.90        VPE ST $/GJ=   .00
```

```
T=300.     P=12.1     V/F=.800     FC=.209

1.0  UNITS AT 13.03 m3 EACH      FEED L/M= 706.0
VESS= 1.40 BY  8.39          #1TUBE=5.39 BY  383.
PRACTICAL COIL LENGTH IS ONLY   192. m
COIL VOL(m3)= 2.94           CW FLOW(L/M)=1120.7  PER UNIT
COILS(MJ/H)= 168098.         VPE ST(MJ/H)=       0.
LPE(MJ/H)=  11183.           O2 PLANT($)=12031240.
OP $/Y= 3294136.             CAP $/Y= 2752879.        TOT CAP $=17205490.
HOT WATER $/GJ= 2.89         VPE ST $/GJ=   .00

T=300.     P=12.1     V/F=.900     FC=.236

1.0  UNITS AT  5.79 m3 EACH      FEED L/M= 627.5
VESS= 1.07 BY  6.42          #1TUBE=5.49 BY  390.
PRACTICAL COIL LENGTH IS ONLY   111. m
COIL VOL(m3)= 3.10           CW FLOW(L/M)=1162.1  PER UNIT
COILS(MJ/H)= 174311.         VPE ST(MJ/H)=       0.
LPE(MJ/H)=   4970.           O2 PLANT($)=12031240.
OP $/Y= 3275519.             CAP $/Y= 2678411.        TOT CAP $=16740070.
HOT WATER $/GJ= 2.85         VPE ST $/GJ=   .00


T=310.     P=15.2     V/F=.800     FC=.276

1.0  UNITS AT  8.00 m3 EACH      FEED L/M= 535.5
VESS= 1.19 BY  7.14          #1TUBE=5.86 BY  409.
PRACTICAL COIL LENGTH IS ONLY   130. m
COIL VOL(m3)= 3.52           CW FLOW(L/M)=1273.2  PER UNIT
COILS(MJ/H)= 190974.         VPE ST(MJ/H)=       0.
LPE(MJ/H)=   8765.           O2 PLANT($)=12031240.
OP $/Y= 3323057.             CAP $/Y= 2726824.        TOT CAP $=17042650.
HOT WATER $/GJ= 2.89         VPE ST $/GJ=   .00
```

```
 1.0  UNITS AT  5.39 m3 EACH     FEED L/M= 720.8
 VESS= 1.04 BY  6.27          #1TUBE=5.37 BY  375.
 PRACTICAL COIL LENGTH IS ONLY   108. m
 COIL VOL(m3)= 2.76          CW FLOW(L/M)=1071.9  PER UNIT
 COILS(MJ/H)= 160791.        VPE ST(MJ/H)=       0.
 LPE(MJ/H)=    5899.         O2 PLANT($)=12031240.
 OP $/Y= 3306243.            CAP $/Y= 2738988.         TOT CAP $=17118670.
 HOT WATER $/GJ= 2.89        VPE ST $/GJ=   .00


 T=320.     P=16.6     V/F=.900     FC=.272

 1.0  UNITS AT  3.36 m3 EACH     FEED L/M= 544.2
 VESS=  .89 BY  5.36          #1TUBE=5.90 BY  406.
 PRACTICAL COIL LENGTH IS ONLY    73. m
 COIL VOL(m3)= 3.39          CW FLOW(L/M)=1239.6  PER UNIT
 COILS(MJ/H)= 185936.        VPE ST(MJ/H)=       0.
 LPE(MJ/H)=    4597.         O2 PLANT($)=12031240.
 OP $/Y= 3334893.            CAP $/Y= 2717415.         TOT CAP $=16983840.
 HOT WATER $/GJ= 2.89        VPE ST $/GJ=   .00
Stop - Program terminated.

B>
```